Supporting Information

Tris(4-bromophenyl)aminium hexachloroantimonate Initiated Oxidative Povarov-type Reaction between Glycine Esters and (Cyclopropylidenemethyl)benzenes Using the Counterion as a Chlorine Donor

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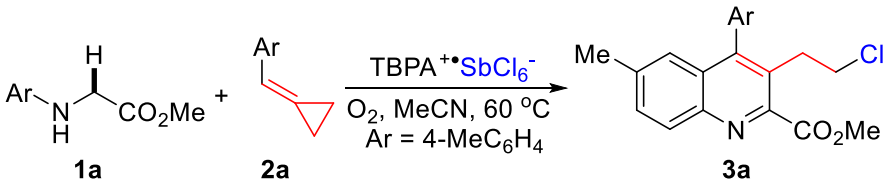
General:

TBPA were purchased from commercial source and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. ^{1}H NMR and ^{13}C NMR (400 MHz, 600MHz and 100 MHz, 150MHz respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard and spin-spin coupling constants (J) are given in Hz. The high resolution mass spectra (HRMS) were measured on an electrospray ionization (ESI) apparatus using time of flight (TOF) mass spectrometry. MCPs were synthesized according to the literature. [1]

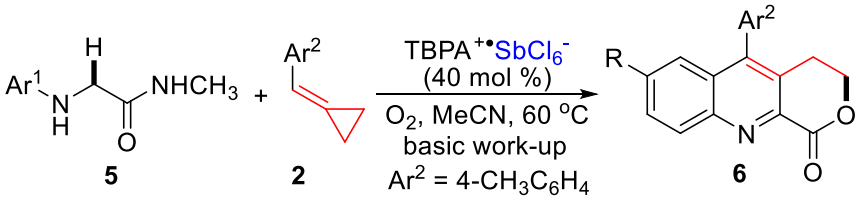
General Experimental Procedure

1. TBPA initiated oxidative Povarov-type reaction of glycine esters



A solution of **1a** (1 mmol, 179 mg) and **2a** (2 mmol, 288 mg) in MeCN (10 mL) was mixed fully, then TBPA (0.4 mmol, 324 mg) was added dropwise under O_2 atmosphere. The reaction solution was stirred under 60 °C (oil bath). After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/ethyl acetate (v/v 5:1) to afford the product.

2. TBPA initiated oxidative Povarov-type reaction of glycine amides



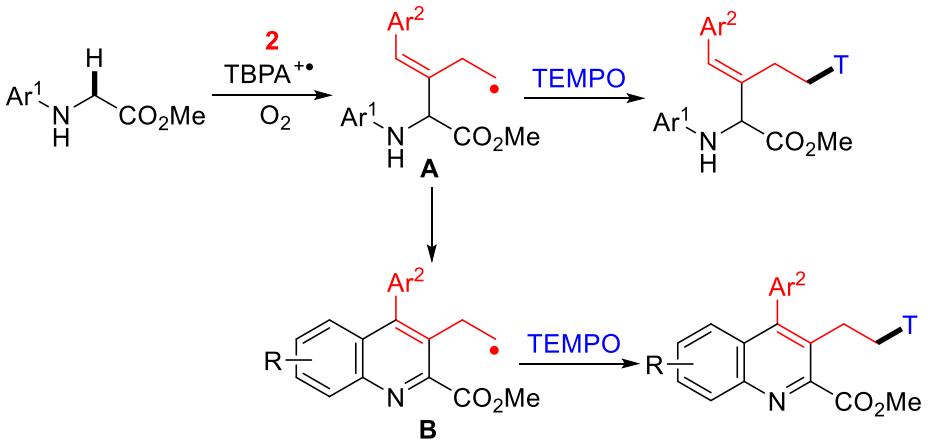
A solution of **5a** (1 mmol, 194 mg) and **2a** (2 mmol, 288 mg) in MeCN (10 mL) was mixed fully, then TBPA (0.4 mmol, 324 mg) was added dropwise under O_2 atmosphere. The reaction solution was stirred under 60 °C (oil bath). After completion monitored by TLC (by UV visualization), triethylamine (1 mL) was added and the reaction solution was stirred for 0.5 hour. Then, the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/ethyl acetate (v/v 2:1) to afford the product.

Mechanistic study

1. TEMPO trapping experiment

A solution of **1a** (0.5 mmol) and **2a** (1 mmol) in MeCN (5 mL) was mixed fully, then TBPA (0.2 mmol) was added dropwise under O_2 atmosphere. When the reaction occurred by TLC detection, 2 equivalent of TEMPO was added. Then, the intermediates was detected by HRMS.

We are delighted to observe the signals at m/z 479.3270 (calcd for $C_{30}H_{42}N_2O_3 + H^+$, 479.3268) and 475.2950 (calcd for $C_{30}H_{38}N_2O_3 + H^+$, 479.2955); this signals are related to the mass of the radical intermediates **A** and **B** trapped by TEMPO, respectively.



2. The oxidative Povarov-type reaction in the presence of bromine source

Follow the general experimental procedure in the presence of Bu_4NBr (1 equiv) and NaBr (1 equiv), respectively. Then, the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 20:1) to afford the product. In the presence of Bu_4NBr, the reaction became complicated, and only trace amount of the chlorinated quinoline was isolated. When NaBr was used, the chlorinated product was isolated in 65% yield, and no brominated quinoline was obtained.

3. Catalytic CAN initiated Povarov-type reaction in the presence of $SbCl_3$

A solution of **1a** (0.5 mmol), **2a** (1 mmol), $SbCl_3$ (0.5 mmol) and tris(4-bromophenyl)amine (0.1 mmol) in MeCN (5 mL) was mixed fully, then CAN (0.1 mmol) was added dropwise under O_2 atmosphere. The reaction solution was stirred under 60 °C. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 20:1) to afford the product.

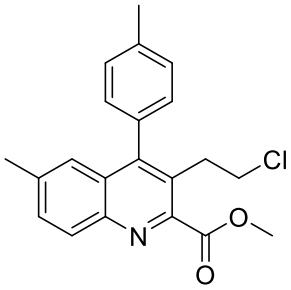
3. $SbCl_3$ initiated reaction under argon atmosphere

A solution of **1a** (0.5 mmol) and **2a** (1 mmol) in MeCN (5 mL) was mixed fully, then $SbCl_3$ (0.5 mmol) was added dropwise under argon atmosphere. The reaction solution was stirred under 60 °C. The reaction was monitored by TLC (by UV visualization), and no reaction occurred. After the solvent was removed under reduced pressure, the starting materials were fully recovered.

References

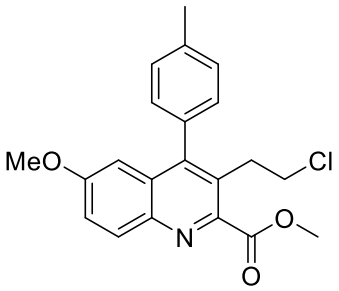
1. (a) Zhu, Z.-Z.; Chen, K.; Yu, L.-Z.; Tang, X.-Y.; Shi, M. *Org. Lett.* **2015**, *17*, 5994; (b) Liu, Y.; Wang, Q.-L.; Zhou, C.-S.; Xiong, B.-Q.; Zhang, P.-L.; Yang, C.-A.; Tang, K.-W. *J. Org. Chem.* **2017**, *82*, 7394; (c) Huang, J.-W.; Shi, M. *J. Org. Chem.* **2005**, *70*, 3859; (d) Fang, W.; Wei, Y.; Shi, M. *Chem. Commun.* **2017**, *53*, 11666.

Analytical data for compounds



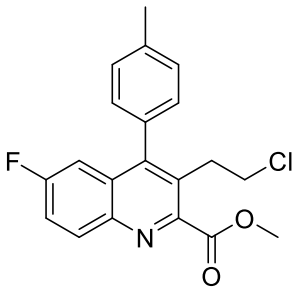
Methyl 3-(2-chloroethyl)-6-methyl-4-(*p*-tolyl)quinoline-2-carboxylate (3a)

Compound **3a** was isolated in 72% yield (254 mg, reddish brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 113-116 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.07 (s, 1H), 4.06 (s, 3H), 3.55 (t, *J* = 7.2 Hz, 2H), 3.24 (t, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 149.7, 148.9, 144.6, 138.5, 138.2, 132.8, 132.2, 129.6, 129.5, 129.0, 128.7, 127.4, 125.1, 53.2, 43.7, 33.1, 21.9, 21.4; HRMS (ESI): Calc'd for $C_{21}H_{20}ClNO_2 + Na^+$, 376.1075; found, 376.1065.



Methyl 3-(2-chloroethyl)-6-methoxy-4-(*p*-tolyl)quinoline-2-carboxylate (3b)

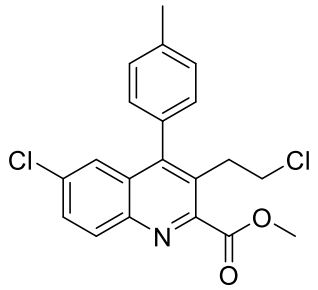
Compound **3b** was isolated in 73% yield (135 mg, yellow solid); column chromatography, silica gel (PE/EA, 10:1); m.p.: 91-95 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.2 Hz, 1H), 7.35 (dd, *J* = 8.2, 4.7 Hz, 3H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.54 (d, *J* = 2.6 Hz, 1H), 4.05 (s, 3H), 3.67 (s, 3H), 3.58 – 3.52 (m, 2H), 3.26 (t, *J* = 7.8 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 159.1, 149.0, 147.0, 142.0, 138.2, 132.9, 131.4, 130.1, 129.6, 128.8, 128.0, 122.6, 104.1, 55.4, 53.2, 43.8, 33.2, 21.4; HRMS (ESI): Calc'd for $C_{21}H_{20}ClNO_3 + Na^+$, 392.1024; found, 392.1034.



Methyl 3-(2-chloroethyl)-6-fluoro-4-(*p*-tolyl)quinoline-2-carboxylate (3c)

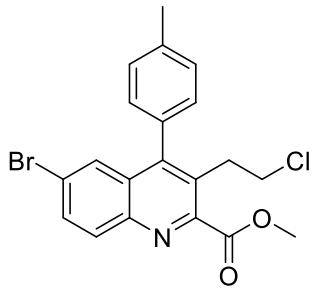
Compound **3c** was isolated in 54% yield (97 mg, yellow solid); column chromatography, silica gel (PE/EA, 10:1); m.p.: 79-81 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 9.2, 5.5 Hz, 1H), 7.47 (td, *J* = 9.2, 2.8 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.94 (dd, *J* = 10.0, 2.7 Hz, 1H), 4.07 (s, 3H), 3.56 (t, *J* = 7.7 Hz, 2H), 3.28 (t, *J* = 7.7 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 161.5 (d, J_{CF} = 250.6 Hz), 149.7 (d, J_{CF} = 62.9 Hz), 143.0, 138.7, 132.6 (d, J_{CF} = 9.4 Hz), 132.2,

129.8 (d, J_{CF} = 9.9 Hz), 129.7, 128.8, 128.1, 120.3 (d, J_{CF} = 26.2 Hz), 109.8 (d, J_{CF} = 23.2 Hz), 53.3, 43.6, 33.0, 21.4; HRMS (ESI): Calc'd for $C_{20}H_{17}ClFNO_2 + Na^+$, 380.0824; found, 380.0834.



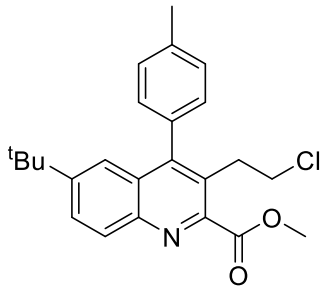
Methyl 6-chloro-3-(2-chloroethyl)-4-(*p*-tolyl)quinoline-2-carboxylate (3d)

Compound **3d** was isolated in 28% yield (53 mg, dark brown solid); column chromatography, silica gel (PE/EA, 10:1); m.p.: 80-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.0 Hz, 1H), 7.63 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 2.2 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.07 (s, 3H), 3.55 (t, *J* = 7.7 Hz, 2H), 3.26 (dd, *J* = 7.7 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 150.3, 149.8, 144.3, 138.7, 134.3, 131.9, 131.5, 129.7, 129.6, 129.4, 128.9, 128.3, 125.3, 53.3, 43.5, 33.0, 21.4; HRMS (ESI): Calc'd for $C_{20}H_{17}Cl_2NO_2 + Na^+$, 396.0529; found, 396.0531.



Methyl 6-bromo-3-(2-chloroethyl)-4-(*p*-tolyl)quinoline-2-carboxylate (3e)

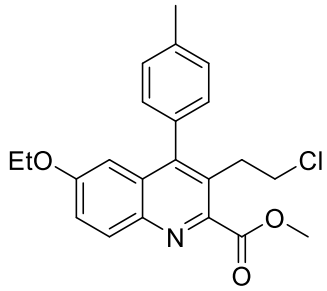
Compound **3e** was isolated in 32% yield (67 mg, yellow solid); column chromatography, silica gel (PE/EA, 10:1); m.p.: 112-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.77 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.07 (s, 3H), 3.54 (t, *J* = 7.7 Hz, 2H), 3.26 (t, *J* = 7.7 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 150.4, 149.7, 144.5, 138.7, 133.4, 131.8, 131.5, 129.8, 129.7, 128.9, 128.5, 128.3, 122.8, 53.3, 43.5, 32.9, 21.4; HRMS (ESI): Calc'd for $C_{20}H_{17}BrClNO_2 + Na^+$, 440.0023; found, 440.0028.



Methyl 6-(*tert*-butyl)-3-(2-chloroethyl)-4-(*p*-tolyl)quinoline-2-carboxylate (3f)

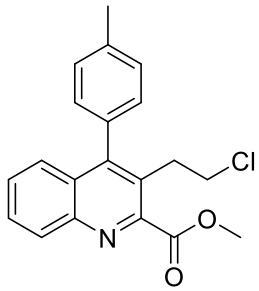
Compound **3f** was isolated in 63% yield (125 mg, yellow solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 132-136 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.9 Hz, 1H), 7.84 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 1.4 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.11 (s, 3H),

3.59 (t, J = 7.8 Hz, 2H), 3.31 (t, J = 8.1 Hz, 2H), 2.53 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 151.3, 150.3, 149.3, 144.6, 138.2, 132.8, 129.4 (two ^{13}C), 129.0, 128.8, 128.4, 127.3, 121.3, 53.2, 43.8, 35.2, 33.1, 31.0, 21.4; HRMS (ESI): Calc'd for $C_{24}H_{26}ClNO_2$ + Na^+, 418.1544; found, 418.1546.



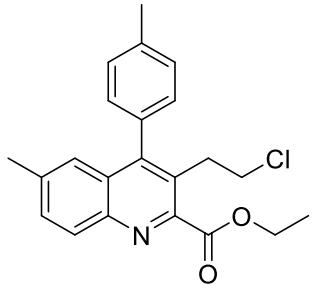
Methyl 3-(2-chloroethyl)-6-ethoxy-4-(*p*-tolyl)quinoline-2-carboxylate (3g)

Compound **3g** was isolated in 65% yield (125 mg, reddish brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 106-108 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 9.2 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.11 (d, J = 7.9 Hz, 2H), 6.53 (d, J = 2.6 Hz, 1H), 4.05 (s, 3H), 3.86 (d, J = 7.0 Hz, 2H), 3.60 – 3.49 (m, 2H), 3.30 – 3.21 (m, 2H), 2.47 (s, 3H), 1.34 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 158.5, 148.9, 146.9, 142.0, 138.2, 133.0, 131.5, 130.2, 129.6, 128.9, 127.9, 122.7, 104.9, 63.6, 53.1, 43.8, 33.2, 21.4, 14.5; HRMS (ESI): Calc'd for $C_{22}H_{22}ClNO_3$ + Na^+, 406.1180; found, 406.1197.



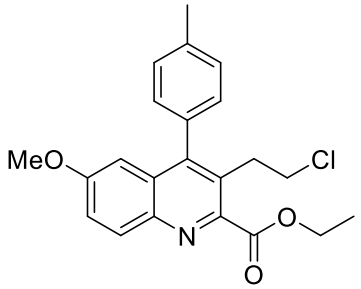
Methyl 3-(2-chloroethyl)-4-(p-tolyl)quinoline-2-carboxylate (3h)

Compound **3h** was isolated in 22% yield (38 mg, yellow solid); column chromatography, silica gel (PE/EA, 10:1); m.p.: 71-74 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.5 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.8 Hz, 3H), 7.11 (d, J = 7.9 Hz, 2H), 4.06 (s, 3H), 3.59 – 3.51 (t, J = 7.8 Hz, 2H), 3.25 (t, J = 7.8 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 150.4, 150.1, 145.9, 138.3, 132.6, 129.9, 129.8, 129.4, 128.9, 128.6, 128.1, 127.2, 126.4, 53.2, 43.6, 33.0, 21.3; HRMS (ESI): Calc'd for $C_{20}H_{18}ClNO_2$+Na^+, 362.0918 found, 362.0928.



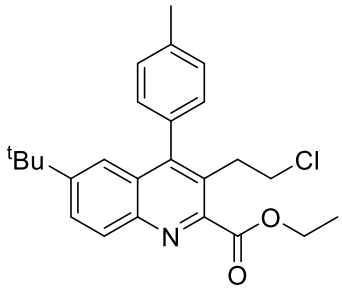
Ethyl 3-(2-chloroethyl)-6-methyl-4-(*p*-tolyl)quinoline-2-carboxylate (3i)

Compound **3i** was isolated in 70% yield (129 mg, dark brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 88-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.07 (s, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 3.60 – 3.49 (m, 2H), 3.27 – 3.16 (m, 2H), 2.47 (s, 3H), 2.37 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 149.9, 149.5, 144.6, 138.3, 138.2, 132.8, 132.1, 129.6, 129.5, 128.9, 128.5, 126.8, 125.1, 62.3, 43.5, 33.3, 21.9, 21.4, 14.3; HRMS (ESI): Calc'd for $C_{22}H_{22}ClNO_2 + Na^+$, 390.1231; found, 390.1237.



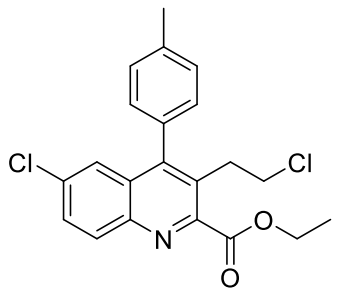
Ethyl 3-(2-chloroethyl)-6-methoxy-4-(*p*-tolyl)quinoline-2-carboxylate (3j)

Compound **3j** was isolated in 65% yield (125 mg, yellow solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 95-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.2 Hz, 1H), 7.33 (d, *J* = 7.3 Hz, 3H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.53 (d, *J* = 2.7 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 3H), 3.59 – 3.49 (m, 2H), 3.27 – 3.16 (m, 2H), 2.47 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 158.9, 148.8, 148.0, 142.1, 138.2, 132.9, 131.5, 129.9, 129.6, 128.8, 127.4, 122.4, 104.1, 62.2, 55.4, 43.6, 33.3, 21.4, 14.3; HRMS (ESI): Calc'd for $C_{22}H_{22}ClNO_3 + Na^+$, 406.1180; found, 406.1196.



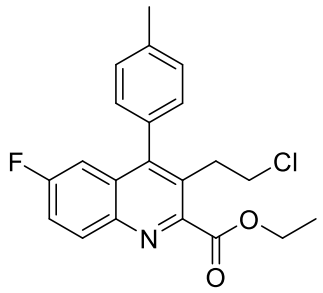
Ethyl 6-(*tert*-butyl)-3-(2-chloroethyl)-4-(*p*-tolyl)quinoline-2-carboxylate (3k)

Compound **3k** was isolated in 66% yield (135 mg, yellow solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 130-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.9 Hz, 1H), 7.79 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 2.6 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.55 (q, *J* = 7.1 Hz, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.24 (t, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 151.0, 150.2, 150.1, 144.6, 138.1, 132.8, 129.4 (two ^{13}C), 128.9, 128.7, 128.2, 126.6, 121.3, 62.2, 43.6, 35.1, 33.3, 31.0, 21.4, 14.3; HRMS (ESI): Calc'd for $C_{25}H_{28}ClNO_2 + Na^+$, 432.1701; found, 432.1703.



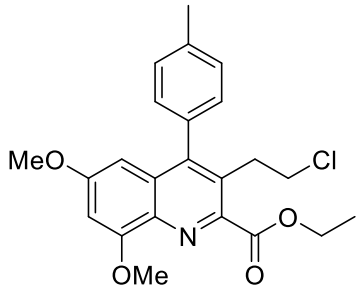
Ethyl 6-chloro-3-(2-chloroethyl)-4-(*p*-tolyl)quinoline-2-carboxylate (3l)

Compound **3l** was isolated in 46% yield (89 mg, reddish brown solid); column chromatography, silica gel (PE/EA, 10:1); m.p.: 55-59 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 4.54 (q, *J* = 7.1 Hz, 2H), 3.53 (t, *J* = 7.8 Hz, 2H), 3.22 (t, *J* = 7.8 Hz, 2H), 2.47 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 151.1, 149.5, 144.4, 138.7, 134.1, 131.9, 131.5, 130.7, 129.7, 129.3, 128.9, 127.7, 125.2, 62.5, 43.3, 33.1, 21.4, 14.2; HRMS (ESI): Calc'd for $C_{21}H_{19}Cl_2NO_2 + Na^+$, 410.0685; found, 410.0695.



Ethyl 3-(2-chloroethyl)-6-fluoro-4-(p-tolyl)quinoline-2-carboxylate (3m)

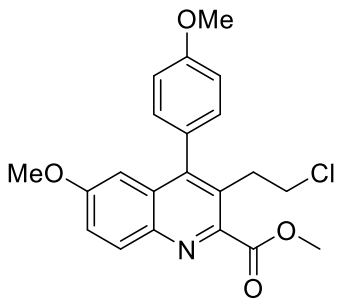
Compound **3m** was isolated in 50% yield (93 mg, dark brown solid); column chromatography, silica gel (PE/EA, 10:1); m.p.: 66-68 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 9.2, 5.4 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.95 (m, 1H), 4.60 (q, *J* = 7.1 Hz, 1H), 3.61 – 3.54 (m, 2H), 3.30 – 3.24 (m, 2H), 2.52 (s, 3H), 1.53 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 161.4 (d, J_{CF} = 250.2 Hz), 150.3 (d, J_{CF} = 2.9 Hz), 149.8 (d, *J* = 5.9 Hz), 143.2, 138.7, 132.6 (d, J_{CF} = 9.4 Hz), 132.2, 129.7, 128.9, 128.8, 127.5, 120.2 (d, J_{CF} = 26.1 Hz), 109.8 (d, J_{CF} = 23.3 Hz), 62.5, 43.4, 33.2, 21.4, 14.3; HRMS (ESI): Calc'd for $C_{21}H_{19}ClFNO_2 + Na^+$, 394.0981 found, 394.0983.



Ethyl 3-(2-chloroethyl)-6,8-dimethoxy-4-(p-tolyl)quinoline-2-carboxylate (3n)

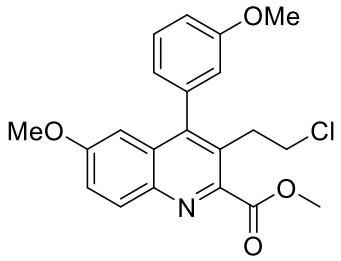
Compound **3n** was isolated in 57% yield (118 mg, dark brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 129-133 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.65 (s, 1H), 6.09 (s, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 3.61 (s, 3H), 3.53 (t, *J* = 7.8

Hz, 2H), 3.29 – 3.18 (m, 2H), 2.44 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 159.6, 156.6, 148.7, 146.3, 138.1, 134.9, 133.3, 130.9, 129.5, 128.8, 128.5, 101.2, 95.9, 62.1, 56.2, 55.3, 43.6, 33.3, 21.4, 14.2; HRMS (ESI): Calc'd for $C_{23}H_{24}ClNO_4$ + Na^+, 436.1286 found, 436.1295.



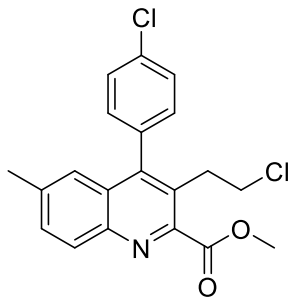
Methyl 3-(2-chloroethyl)-6-methoxy-4-(4-methoxyphenyl)quinoline-2-carboxylate (3o)

Compound **3o** was isolated in 42% yield (81 mg, dark brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.2 Hz, 1H), 7.35 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.56 (d, *J* = 2.6 Hz, 1H), 4.05 (s, 3H), 3.91 (s, 3H), 3.68 (s, 3H), 3.56 (t, *J* = 7.6 Hz, 2H), 3.28 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 159.5, 159.1, 148.7, 146.5, 142.1, 131.5, 130.4, 130.2, 128.3, 128.0, 122.5, 114.3, 104.0, 55.3, 53.2, 43.7, 33.2, 30.2; HRMS (ESI): Calc'd for $C_{21}H_{20}ClNO_4$ + Na^+, 408.0973 found, 408.0985.



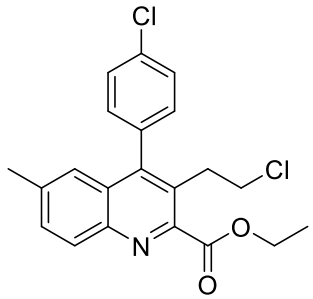
Methyl 3-(2-chloroethyl)-6-methoxy-4-(3-methoxyphenyl)quinoline-2-carboxylate (3p)

Compound **3p** was isolated in 50% yield (96 mg, dark brown oil); column chromatography, silica gel (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.2 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.35 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 6.78 (s, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 4.05 (s, 3H), 3.83 (s, 3H), 3.67 (s, 3H), 3.60 – 3.56 (m, 2H), 3.31 – 3.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 159.8, 159.2, 148.6, 146.9, 142.0, 137.3, 131.5, 130.1, 129.8, 127.8, 122.6, 121.4, 114.6, 114.0, 104.1, 55.4, 53.2, 43.8, 33.2; HRMS (ESI): Calc'd for $C_{21}H_{20}ClNO_4$ + Na^+, 408.0973 found, 408.0985.



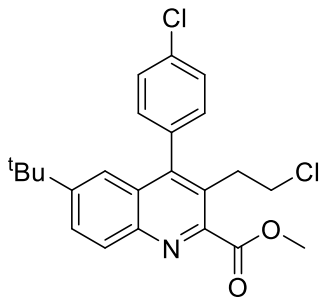
Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-methylquinoline-2-carboxylate (3q)

Compound **3q** was isolated in 37% yield (70 mg, dark brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 91-94 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.00 (s, 1H), 4.05 (s, 3H), 3.54 (t, *J* = 7.6 Hz, 2H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 148.8, 148.2, 144.5, 139.0, 134.6, 134.3, 132.4, 130.6, 129.8, 129.1, 128.3, 127.4, 124.7, 53.2, 43.6, 33.0, 21.9; HRMS (ESI): Calc'd for $C_{20}H_{17}Cl_2NO_2 + Na^+$, 396.0529 found, 396.0538.



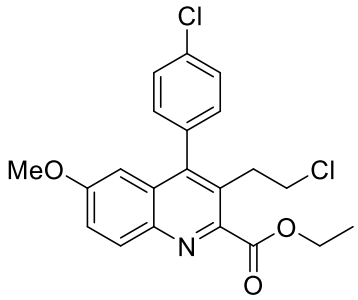
Ethyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-methylquinoline-2-carboxylate (3r)

Compound **3r** was isolated in 48% yield (93 mg, reddish brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 142-147 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 3H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.99 (s, 1H), 4.53 (q, *J* = 7.2 Hz, 2H), 3.53 (t, *J* = 7.8 Hz, 2H), 3.24 – 3.15 (m, 2H), 2.38 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 149.7, 147.9, 144.6, 138.7, 134.6, 134.4, 132.3, 130.6, 129.7, 129.1, 128.1, 126.8, 124.7, 62.4, 43.4, 33.1, 21.9, 14.2; HRMS (ESI): Calc'd for $C_{21}H_{19}Cl_2NO_2 + Na^+$, 410.0685 found, 410.0694.



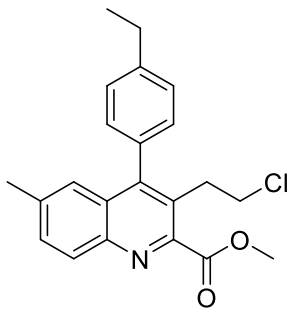
Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(4-chlorophenyl)quinoline-2-carboxylate (3s)

Compound **3s** was isolated in 55% yield (115 mg, reddish brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 141-143 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.9 Hz, 1H), 7.82 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 1.9 Hz, 1H), 4.06 (s, 3H), 3.55 (t, *J* = 7.6 Hz, 2H), 3.25 (t, *J* = 7.6 Hz, 2H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 151.7, 149.1, 148.7, 144.5, 134.6, 134.4, 130.6, 129.6, 129.1, 129.0, 127.9, 127.3, 120.8, 53.2, 43.6, 35.2, 32.9, 30.9; HRMS (ESI): Calc'd for $C_{23}H_{23}Cl_2NO_2 + Na^+$, 438.0998 found, 438.1007.



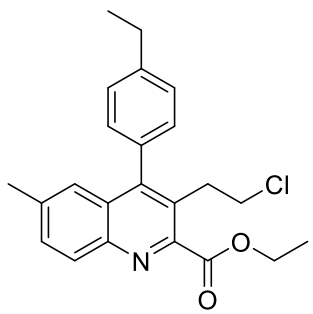
Ethyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-methoxyquinoline-2-carboxylate (3t)

Compound **3t** was isolated in 39% yield (79 mg, yellow oil); column chromatography, silica gel (PE/EA, 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.2 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.38 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.24 – 7.20 (m, 2H), 6.47 (d, *J* = 2.7 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 3.60 – 3.53 (m, 2H), 3.27 – 3.20 (m, 2H), 1.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 159.3, 147.9, 147.2, 142.2, 134.7, 134.6, 131.8, 130.6, 129.6, 129.3, 127.4, 122.6, 103.7, 62.4, 55.5, 43.5, 33.2, 14.3; HRMS (ESI): Calc'd for $C_{21}H_{19}Cl_2NO_3 + Na^+$, 426.0634 found, 426.0644.



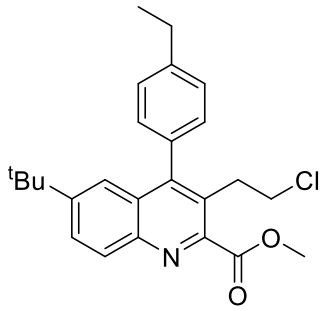
Methyl 3-(2-chloroethyl)-4-(4-ethylphenyl)-6-methylquinoline-2-carboxylate (3u)

Compound **3u** was isolated in 73% yield (135 mg, dark brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 85-87 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.6 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.06 (s, 1H), 4.03 (s, 3H), 3.53 (t, *J* = 7.8 Hz, 2H), 3.23 (t, *J* = 7.8 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.35 (s, 3H), 1.32 (q, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 149.7, 149.0, 144.6, 144.4, 138.4, 133.0, 132.1, 129.6, 129.0, 128.7, 128.2, 127.4, 125.1, 53.1, 43.7, 33.1, 28.6, 21.9, 15.2; HRMS (ESI): Calc'd for $C_{22}H_{22}ClNO_2 + Na^+$, 390.1231 found, 390.1241.



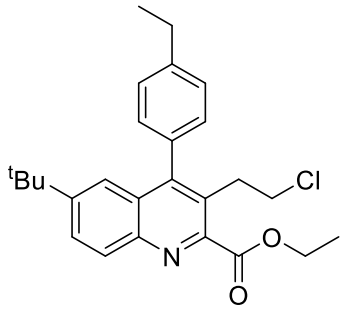
Ethyl 3-(2-chloroethyl)-4-(4-ethylphenyl)-6-methylquinoline-2-carboxylate (3v)

Compound **3v** was isolated in 67% yield (128 mg, yellow solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 73-75 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.18 – 7.11 (m, 2H), 7.09 (s, 1H), 4.61 – 4.51 (m, 2H), 3.56 (t, *J* = 7.1 Hz, 2H), 3.23 (t, *J* = 7.2 Hz, 2H), 2.79 (q, *J* = 7.0 Hz, 2H), 2.38 (s, 3H), 1.48 (t, *J* = 6.8 Hz, 3H), 1.35 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 149.9, 149.5, 144.7, 144.4, 138.2, 133.0, 132.0, 129.6, 129.0, 128.5, 128.2, 126.8, 125.1, 62.3, 43.5, 33.3, 28.6, 21.9, 15.3, 14.3; HRMS (ESI): Calc'd for $C_{23}H_{24}ClNO_2 + Na^+$, 404.1388 found, 404.1394.



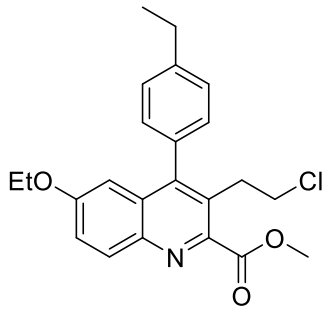
Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(4-ethylphenyl)quinoline-2-carboxylate (3w)

Compound **3w** was isolated in 67% yield (138 mg, yellow solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 111-116 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.9 Hz, 1H), 7.78 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 1.9 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.04 (s, 3H), 3.55 (t, *J* = 7.8 Hz, 2H), 3.27 (t, *J* = 7.8 Hz, 2H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 151.2, 150.3, 149.3, 144.5, 144.4, 133.0, 129.4, 129.0, 128.7, 128.4, 128.1, 127.2, 121.3, 53.1, 43.7, 35.1, 33.1, 30.9, 28.6, 15.3; HRMS (ESI): Calc'd for $C_{25}H_{28}ClNO_2 + Na^+$, 432.1701 found, 432.1704.



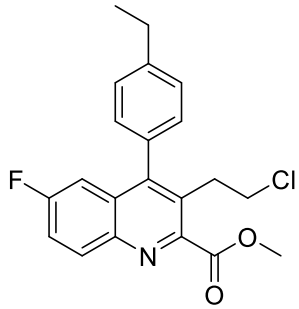
Ethyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(4-ethylphenyl)quinoline-2-carboxylate (3x)

Compound **3x** was isolated in 59% yield (125 mg, reddish brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 109-113 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.9 Hz, 1H), 7.78 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.25 (s, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.53 (q, *J* = 7.1 Hz, 2H), 3.58 – 3.50 (m, 2H), 3.27 – 3.19 (m, 2H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.6 Hz, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 151.3, 150.5, 150.4, 144.9, 144.7, 133.3, 129.7, 129.3, 129.0, 128.5, 128.4, 126.9, 121.6, 62.5, 43.9, 35.4, 33.6, 31.2, 29.0, 15.6, 14.6; HRMS (ESI): Calc'd for $C_{26}H_{30}ClNO_2 + Na^+$, 446.1857 found, 446.1859.



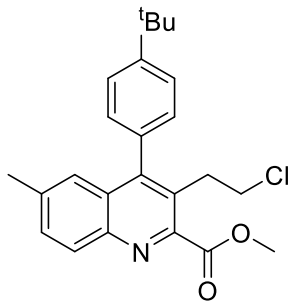
Methyl 3-(2-chloroethyl)-6-ethoxy-4-(4-ethylphenyl)quinoline-2-carboxylate (3y)

Compound **3y** was isolated in 61% yield (121 mg, dark brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 79-85 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.2 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.52 (d, *J* = 2.2 Hz, 1H), 4.03 (s, 3H), 3.85 (q, *J* = 6.9 Hz, 2H), 3.54 (t, *J* = 7.8 Hz, 2H), 3.25 (t, *J* = 7.8 Hz, 2H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 158.4, 148.9, 147.0, 144.4, 142.0, 133.2, 131.4, 130.2, 128.9, 128.3, 127.9, 122.6, 105.0, 63.6, 53.1, 43.8, 33.2, 28.6, 15.2, 14.5; HRMS (ESI): Calc'd for $C_{23}H_{24}ClNO_3 + Na^+$, 420.1337 found, 420.1342.



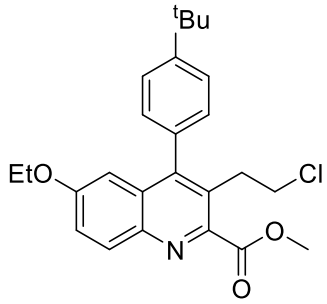
Methyl 3-(2-chloroethyl)-4-(4-ethylphenyl)-6-fluoroquinoline-2-carboxylate (3z)

Compound **3z** was isolated in 41% yield (76 mg, dark brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 98-101 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 9.1, 5.4 Hz, 1H), 7.44 (dd, *J* = 12.0, 5.0 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 6.93 (dd, *J* = 9.8, 1.9 Hz, 1H), 4.05 (s, 3H), 3.54 (t, *J* = 7.6 Hz, 2H), 3.27 (t, *J* = 7.6 Hz, 2H), 2.76 (q, *J* = 7.5 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 161.5 (d, J_{CF} = 250.5 Hz), 150.0 (d, J_{CF} = 5.6 Hz), 149.5 (d, J_{CF} = 3.5 Hz), 144.9, 143.0, 132.6 (d, J_{CF} = 9.4 Hz), 132.4, 129.9 (d, *J* = 9.9 Hz), 128.9, 128.4, 128.2, 120.3 (d, J_{CF} = 26.3 Hz), 109.9 (d, J_{CF} = 23.3 Hz), 53.2, 43.6, 33.0, 28.7, 15.3; HRMS (ESI): Calc'd for $C_{21}H_{19}ClFNO_2 + Na^+$, 394.0981 found, 394.0989.



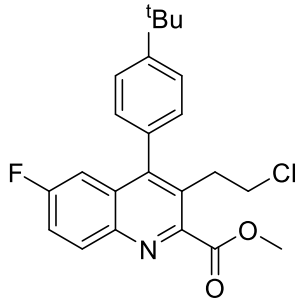
Methyl 4-(4-(tert-butyl)phenyl)-3-(2-chloroethyl)-6-methylquinoline-2-carboxylate (4a)

Compound **4a** was isolated in 63% yield (125 mg, yellow solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 96-98 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 1H), 7.54 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 1H), 4.06 (s, 3H), 3.56 (t, *J* = 7.8 Hz, 2H), 3.26 (t, *J* = 7.8 Hz, 2H), 2.39 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 151.4, 149.7, 149.1, 144.6, 138.4, 132.8, 132.1, 129.6, 128.8, 128.7, 127.4, 125.6, 125.2, 53.1, 43.8, 34.8, 33.1, 31.4, 22.0; HRMS (ESI): Calc'd for $C_{24}H_{26}ClNO_2 + Na^+$, 418.1544 found, 418.1552.



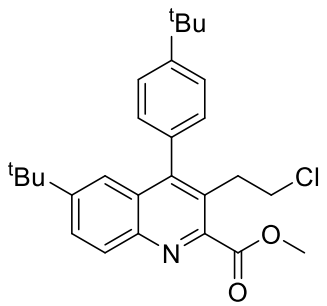
Methyl 4-(4-(tert-butyl)phenyl)-3-(2-chloroethyl)-6-ethoxyquinoline-2-carboxylate (4b)

Compound **4b** was isolated in 44% yield (94 mg, dark brown solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 99-102 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.2 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.36 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.54 (d, *J* = 2.5 Hz, 1H), 4.06 (s, 3H), 3.89 (q, *J* = 6.9 Hz, 2H), 3.57 (t, *J* = 7.8 Hz, 2H), 3.27 (t, *J* = 7.8 Hz, 2H), 1.42 (s, 9H), 1.34 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 158.4, 151.4, 148.9, 147.1, 142.0, 133.0, 131.5, 130.2, 128.7, 127.9, 125.7, 122.4, 105.3, 63.6, 53.1, 43.8, 34.8, 33.2, 31.4, 14.5; HRMS (ESI): Calc'd for $C_{25}H_{28}ClNO_3 + Na^+$, 448.1650 found, 448.1656.



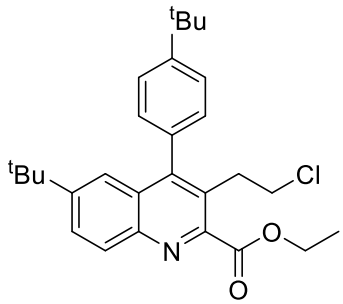
Methyl 4-(4-(tert-butyl)phenyl)-3-(2-chloroethyl)-6-fluoroquinoline-2-carboxylate (4c)

Compound **4c** was isolated in 65% yield (130 mg, yellow solid); column chromatography, silica gel (PE/EA, 10:1); m.p.: 106-109 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 9.2, 5.4 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.94 (dd, *J* = 10.0, 2.6 Hz, 1H), 4.07 (s, 3H), 3.55 (t, *J* = 7.6 Hz, 2H), 3.28 (t, *J* = 7.6 Hz, 2H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 161.5 (d, *J* = 250.5 Hz), 151.8, 150.0 (d, *J* = 5.9 Hz), 149.5 (d, *J* = 3.1 Hz), 143.0, 132.5 (d, *J* = 9.4 Hz), 132.1, 129.9 (d, *J* = 9.9 Hz), 128.7, 128.2, 125.8, 120.2 (d, *J* = 26.1 Hz), 109.9 (d, *J* = 23.3 Hz), 53.2, 43.6, 34.8, 32.9, 31.3; HRMS (ESI): Calc'd for $C_{23}H_{23}ClFNO_2 + Na^+$, 422.1294 found, 422.1301.



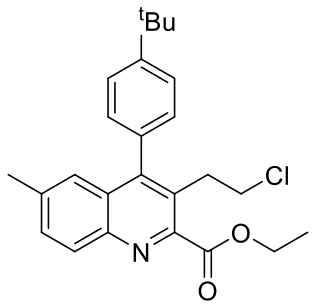
Methyl 6-(tert-butyl)-4-(4-(tert-butyl)phenyl)-3-(2-chloroethyl)quinoline-2-carboxylate (4d)

Compound **4d** was isolated in 57% yield (125 mg, yellow solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 117-120 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.24 (s, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 4.08 (s, 3H), 3.59 (t, *J* = 7.5 Hz, 2H), 3.32 (t, *J* = 7.4 Hz, 2H), 1.44 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 151.4, 151.2, 150.4, 149.3, 144.6, 132.8, 129.4, 128.9, 128.8, 128.5, 127.3, 125.5, 121.3, 53.2, 43.9, 35.1, 34.8, 33.1, 31.4, 30.9; HRMS (ESI): Calc'd for $C_{27}H_{32}ClNO_2 + Na^+$, 460.2014 found, 460.2021.



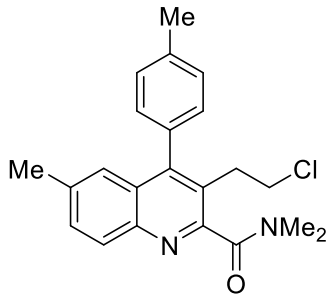
Ethyl 6-(tert-butyl)-4-(4-(tert-butyl)phenyl)-3-(2-chloroethyl)quinoline-2-carboxylate (4e)

Compound **4e** was isolated in 67% yield (152 mg, yellow solid); column chromatography, silica gel (PE/EA, 5:1); m.p.: 125-129 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.9 Hz, 1H), 7.78 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 1.8 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 4.54 (q, *J* = 7.1 Hz, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 3.25 (t, *J* = 7.8 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.41 (s, 9H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 151.4, 150.9, 150.2, 150.1, 144.6, 132.8, 129.4, 128.8, 128.6, 128.3, 126.6, 125.5, 121.2, 62.2, 43.6, 35.1, 34.8, 33.3, 31.3, 30.9, 14.3; HRMS (ESI): Calc'd for $C_{28}H_{34}ClNO_2 + Na^+$, 474.2170 found, 474.2182.



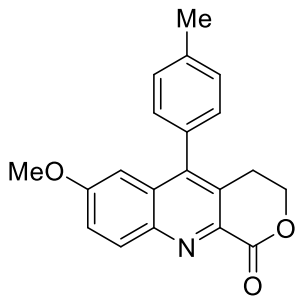
Ethyl 4-(4-(tert-butyl)phenyl)-3-(2-chloroethyl)-6-methylquinoline-2-carboxylate (4f)

Compound **4f** was isolated in 60% yield (123 mg, dark brown oil); column chromatography, silica gel (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.08 (s, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 3.55 (t, *J* = 7.8 Hz, 2H), 3.22 (t, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 151.4, 149.9, 149.6, 144.6, 138.2, 132.8, 132.1, 129.5, 128.8, 128.6, 126.8, 125.6, 125.1, 62.3, 43.6, 34.8, 33.2, 31.4, 21.9, 14.2; HRMS (ESI): Calc'd for $C_{25}H_{28}ClNO_2 + Na^+$, 432.1701 found, 432.1708.



3-(2-Chloroethyl)-N,N,6-trimethyl-4-(*p*-tolyl)quinoline-2-carboxamide (4g)

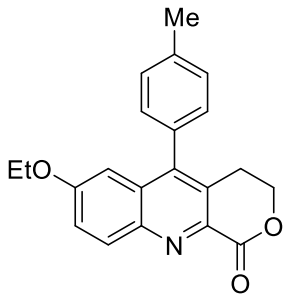
Compound **4g** was isolated in 31% yield (57 mg, dark brown oil); column chromatography, silica gel (PE/EA, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 1H), 7.49 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.09 (s, 1H), 3.52 (t, *J* = 7.6 Hz, 2H), 3.19 (s, 3H), 3.09 (t, *J* = 7.6 Hz, 2H), 2.98 (s, 3H), 2.46 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 154.2, 149.2, 144.5, 138.1, 137.3, 132.8, 131.8, 129.4, 129.0, 128.9, 127.8, 125.9, 125.1, 43.36, 38.69, 34.91, 32.87, 21.79, 21.36; HRMS (ESI): Calc'd for $C_{22}H_{23}ClN_2O + H^+$, 367.1572; found, 367.1579.



7-Methoxy-5-(p-tolyl)-3,4-dihydro-1H-pyrano[3,4-b]quinolin-1-one (6a)

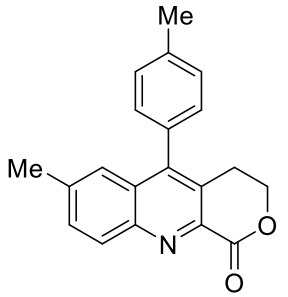
Compound **6a** was isolated in 68% yield (217 mg, dark brown solid); column chromatography, silica gel (PE/EA, 2:1); m.p.: 231-235 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 9.3 Hz, 1H), 7.30 (d, *J* = 7.7

Hz, 3H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.71 (d, *J* = 2.5 Hz, 1H), 4.42 (t, *J* = 5.8 Hz, 2H), 3.66 (s, 3H), 2.91 (t, *J* = 5.8 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 159.9, 145.1, 144.2, 140.4, 138.7, 132.8, 132.0, 130.4, 129.8, 129.6, 129.0, 123.0, 103.4, 67.0, 55.5, 26.7, 21.4; HRMS (ESI): Calc'd for $C_{20}H_{17}NO_3 + Na^+$, 342.1101 found, 342.1102.



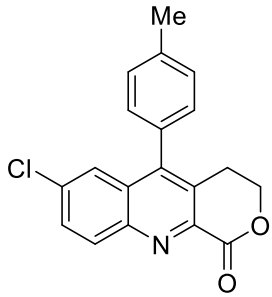
7-Ethoxy-5-(p-tolyl)-3,4-dihydro-1H-pyrano[3,4-b]quinolin-1-one (6b)

Compound **6b** was isolated in 56% yield (93 mg, dark brown solid); column chromatography, silica gel (PE/EA, 2:1); m.p.: 191-196 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.3 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 3H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.71 (d, *J* = 2.6 Hz, 1H), 4.43 (t, *J* = 5.9 Hz, 2H), 3.87 (q, *J* = 6.9 Hz, 3H), 2.92 (t, *J* = 5.8 Hz, 2H), 2.42 (s, 3H), 1.31 (t, *J* = 6.9 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 159.2, 145.0, 144.0, 140.2, 138.5, 132.6, 132.0, 130.3, 129.7, 129.5, 129.0, 123.1, 104.1, 66.9, 63.8, 26.6, 21.3, 14.4; HRMS (ESI): Calc'd for $C_{21}H_{19}NO_3 + Na^+$, 356.1257 found, 356.1263.



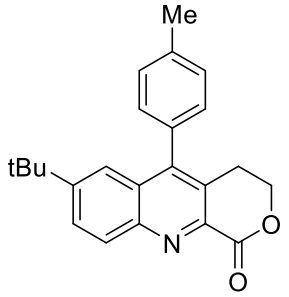
7-Methyl-5-(p-tolyl)-3,4-dihydro-1H-pyrano[3,4-b]quinolin-1-one (6c)

Compound **6c** was isolated in 29% yield (44 mg, yellow solid); column chromatography, silica gel (PE/EA, 2:1); m.p.: 65-68 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 1H), 7.54 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.29 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.48 (t, *J* = 5.9 Hz, 2H), 2.97 (t, *J* = 5.9 Hz, 2H), 2.46 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 146.5, 146.1, 142.0, 139.7, 138.6, 132.3, 131.9, 130.8, 129.6, 129.2, 129.1, 128.8, 124.6, 67.0, 26.6, 22.1, 21.4; HRMS (ESI): Calc'd for $C_{20}H_{17}NO_2 + Na^+$, 326.1157; found, 326.1158.



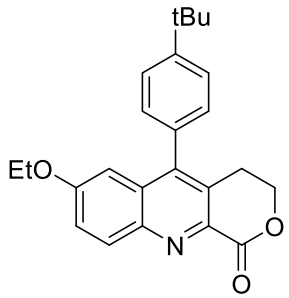
7-Chloro-5-(p-tolyl)-3,4-dihydro-1H-pyrano[3,4-b]quinolin-1-one (6d)

Compound **6d** was isolated in 22% yield (36 mg, dark brown solid); column chromatography, silica gel (PE/EA, 2:1); m.p.: 176-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.0 Hz, 1H), 7.64 (dd, *J* = 9.0, 1.9 Hz, 1H), 7.53 (d, *J* = 2.1 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 4.51 (t, *J* = 5.8 Hz, 2H), 3.02 (t, *J* = 5.8 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 146.4, 146.2, 143.1, 139.1, 135.5, 132.7, 131.1, 131.0, 130.1, 129.8, 129.4, 129.1, 124.8, 67.0, 26.6, 21.4; HRMS (ESI): Calc'd for $C_{19}H_{14}ClNO_2 + Na^+$, 346.0611; found, 346.0614.



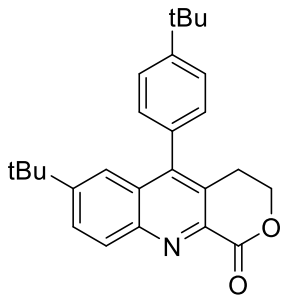
7-(*tert*-Butyl)-5-(*p*-tolyl)-3,4-dihydro-1H-pyrano[3,4-b]quinolin-1-one (6e)

Compound **6e** was isolated in 34% yield (59 mg, yellow solid); column chromatography, silica gel (PE/EA, 2:1); m.p.: 153-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.0 Hz, 1H), 7.82 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.48 (t, *J* = 5.8 Hz, 2H), 2.99 (t, *J* = 5.8 Hz, 2H), 2.46 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 152.3, 146.7, 146.5, 142.3, 138.6, 131.8, 130.6, 129.5, 129.2, 129.1, 129.0, 128.5, 120.7, 67.1, 35.3, 30.9, 26.6, 21.4; HRMS (ESI): Calc'd for $C_{23}H_{23}NO_2 + Na^+$, 368.1627; found, 368.1629.



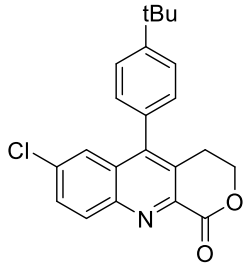
5-(4-(*tert*-Butyl)phenyl)-7-ethoxy-3,4-dihydro-1H-pyrano[3,4-b]quinolin-1-one (6f)

Compound **6f** was isolated in 31% yield (59 mg, dark brown solid); column chromatography, silica gel (PE/EA, 2:1); m.p.: 196-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9.3 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.35 (dd, *J* = 9.3, 2.6 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 2.6 Hz, 1H), 4.47 (t, *J* = 5.8 Hz, 2H), 3.93 (q, *J* = 7.0 Hz, 2H), 2.97 (t, *J* = 5.8 Hz, 2H), 1.54 – 1.26 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 159.2, 151.7, 145.0, 144.1, 140.3, 132.7, 132.0, 130.3, 129.6, 128.9, 125.8, 122.8, 104.5, 67.0, 63.8, 34.8, 31.3, 26.7, 14.5; HRMS (ESI): Calc'd for $C_{24}H_{25}NO_3 + Na^+$, 398.1732; found, 398.1729.



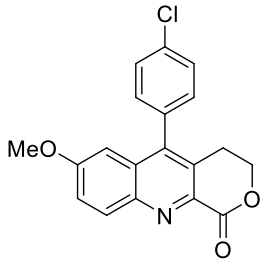
7-(*tert*-Butyl)-5-(4-(*tert*-butyl)phenyl)-3,4-dihydro-1H-pyrano[3,4-b]quinolin-1-one (6g)

Compound **6g** was isolated in 37% yield (72 mg, yellow solid); column chromatography, silica gel (PE/EA, 2:1); m.p.: 225-229 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.50 (s, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 4.48 (t, *J* = 5.7 Hz, 2H), 3.02 (t, *J* = 5.7 Hz, 2H), 1.40 (s, 9H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 152.3, 151.8, 146.7, 146.5, 142.3, 131.8, 130.6, 129.1, 129.1, 129.0, 128.5, 125.7, 120.8, 67.1, 35.3, 34.8, 31.3, 30.9, 26.7; HRMS (ESI): Calc'd for $C_{26}H_{29}NO_2$ + Na^+, 410.2096; found, 410.2092.



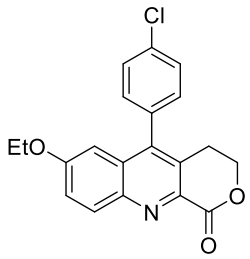
5-(4-(tert-Butyl)phenyl)-7-chloro-3,4-dihydro-1H-pyrano[3,4-b]quinolin-1-one (6h)

Compound **6h** was isolated in 28% yield (52 mg, yellow solid); column chromatography, silica gel (PE/EA, 2:1); m.p.: 245-250 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.0 Hz, 1H), 7.64 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.23 – 7.15 (m, 2H), 4.50 (t, *J* = 5.8 Hz, 2H), 3.03 (t, *J* = 5.8 Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 152.2, 146.4, 146.2, 143.2, 135.4, 132.7, 131.0, 131.0, 130.2, 129.4, 128.9, 126.0, 124.8, 67.0, 34.9, 31.3, 26.7; HRMS (ESI): Calc'd for $C_{22}H_{20}ClNO_2$ + Na^+, 388.1080; found, 388.1077.



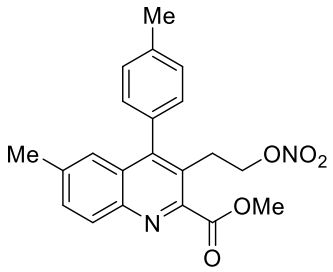
5-(4-Chlorophenyl)-7-methoxy-3,4-dihydro-1H-pyrano[3,4-b]quinolin-1-one (6i)

Compound **6i** was isolated in 35% yield (60 mg, dark brown solid); column chromatography, silica gel (PE/EA, 2:1); m.p.: 178-181 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 9.3 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.35 (dd, *J* = 9.3, 2.6 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 2.6 Hz, 1H), 4.47 (t, *J* = 5.8 Hz, 2H), 3.72 (s, 3H), 2.94 (t, *J* = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 160.1, 144.1, 143.5, 140.3, 134.9, 133.5, 132.8, 130.6, 129.9, 129.5, 129.4, 123.2, 102.9, 66.8, 55.5, 26.6; HRMS (ESI): Calc'd for $C_{19}H_{14}ClNO_3$ + Na^+, 362.0560; found, 362.0560.



5-(4-Chlorophenyl)-7-ethoxy-3,4-dihydro-1H-pyrano[3,4-b]quinolin-1-one (6j)

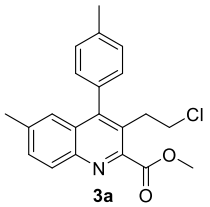
Compound **6j** was isolated in 30% yield (53 mg, dark brown solid); column chromatography, silica gel (PE/EA, 2:1); m.p.: 179-182 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 9.3 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.35 (dd, *J* = 9.3, 2.5 Hz, 1H), 7.27 – 7.02 (m, 2H), 6.63 (d, *J* = 2.4 Hz, 1H), 4.47 (t, *J* = 5.8 Hz, 2H), 3.91 (q, *J* = 7.1 Hz, 2H), 2.93 (t, *J* = 5.8 Hz, 2H), 1.36 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 159.5, 144.0, 143.4, 140.2, 134.9, 133.6, 132.8, 130.6, 130.0, 129.5, 129.4, 123.3, 103.6, 66.8, 63.9, 26.6, 14.5; HRMS (ESI): Calc'd for $C_{20}H_{16}ClNO_3 + Na^+$, 376.0716; found, 376.0714.



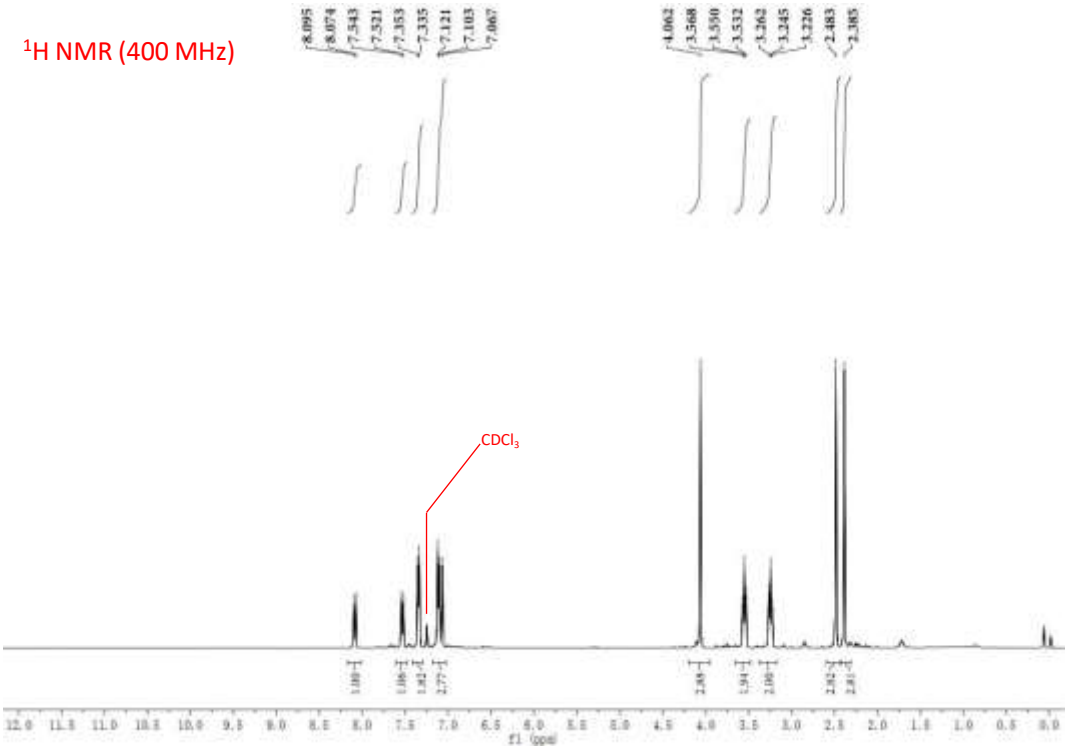
Methyl 6-methyl-3-(2-(nitrooxy)ethyl)-4-(p-tolyl)quinoline-2-carboxylate (7)

Compound **7** was isolated in 22% yield (42 mg, dark brown solid); column chromatography, silica gel (PE/EA, 10:1); m.p.: 49-52 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.08 (s, 1H), 4.51 (t, *J* = 7.0 Hz, 2H), 4.06 (s, 3H), 3.24 (t, *J* = 7.0 Hz, 2H), 2.48 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 150.1, 148.6, 144.7, 138.7, 138.3, 132.7, 132.3, 129.7, 129.5, 128.9, 128.7, 125.7, 125.1, 72.5, 53.2, 27.5, 21.9, 21.4; HRMS (ESI): Calc'd for $C_{21}H_{20}N_2O_5 + Na^+$, 403.1270; found, 403.1270.

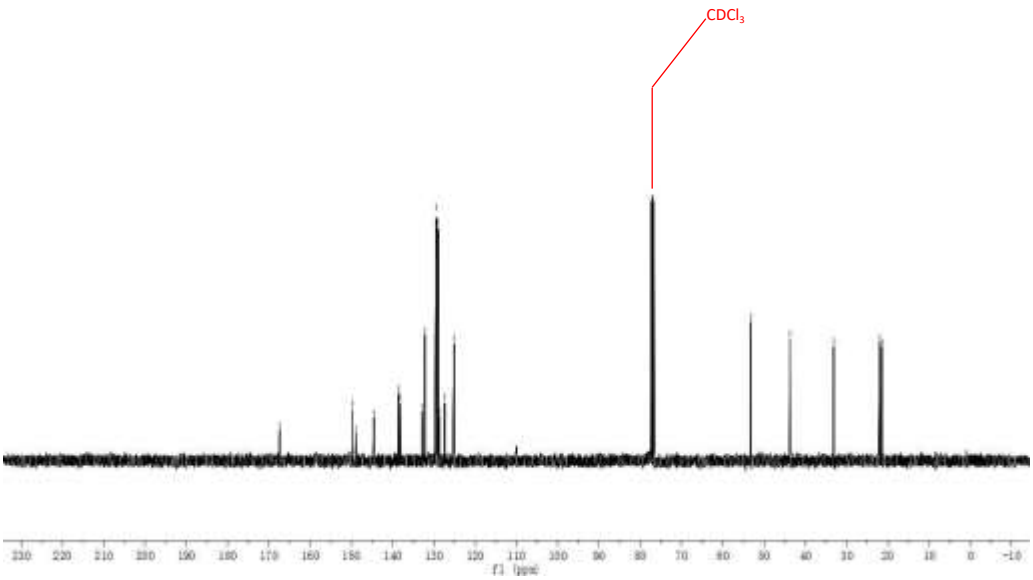
^{1}H and ^{13}C spectra

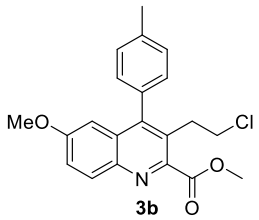


^{1}H NMR (400 MHz)

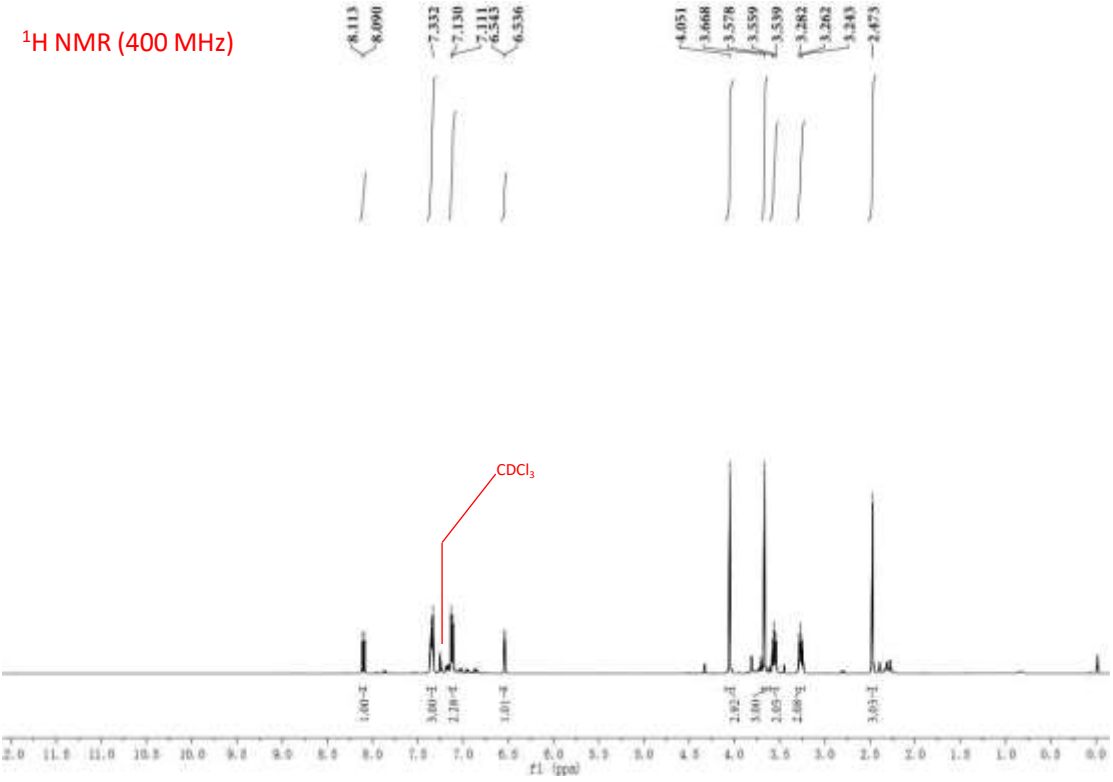


^{13}C NMR (101 MHz)

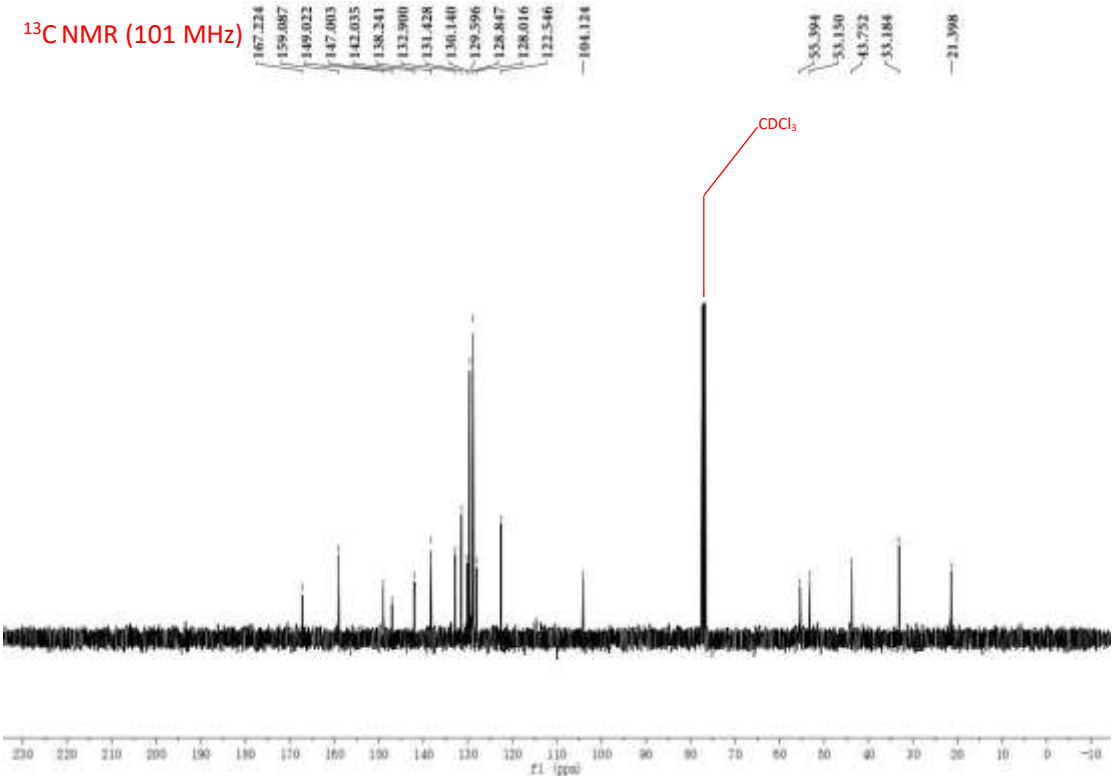


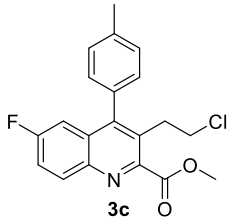


^{1}H NMR (400 MHz)



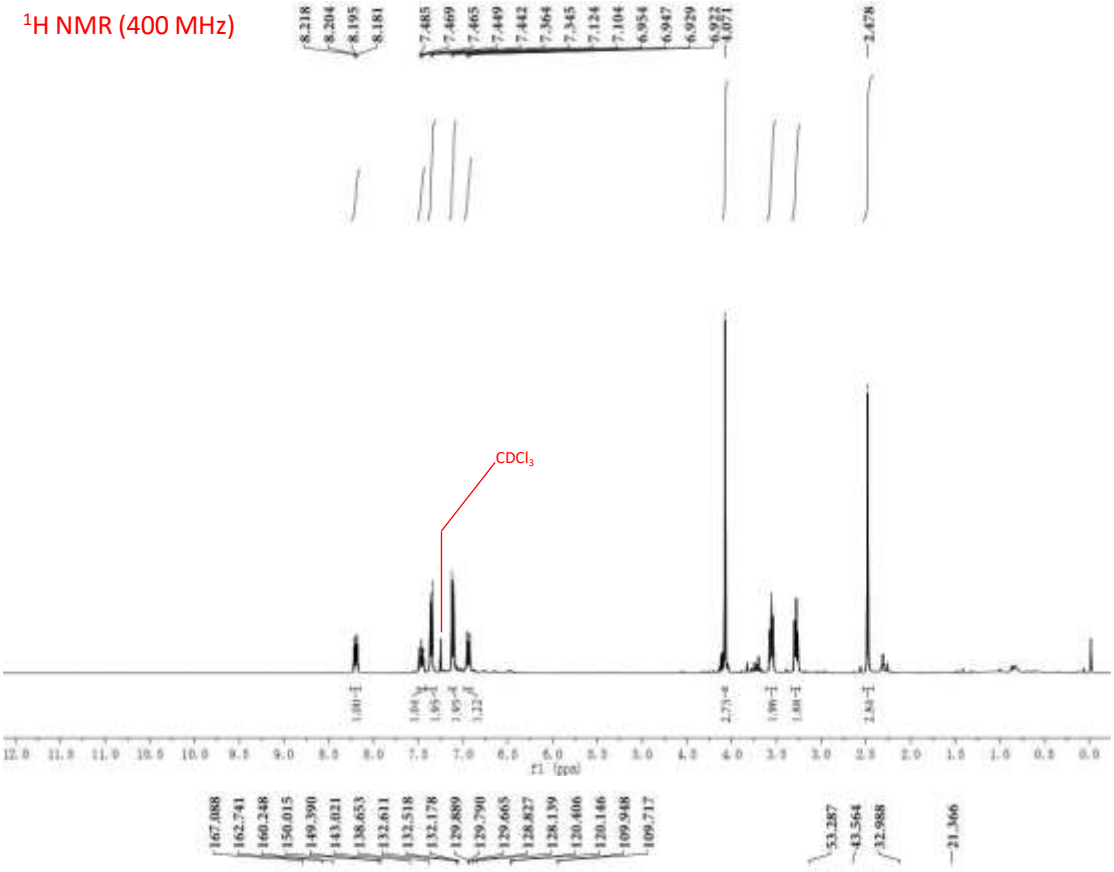
^{13}C NMR (101 MHz)



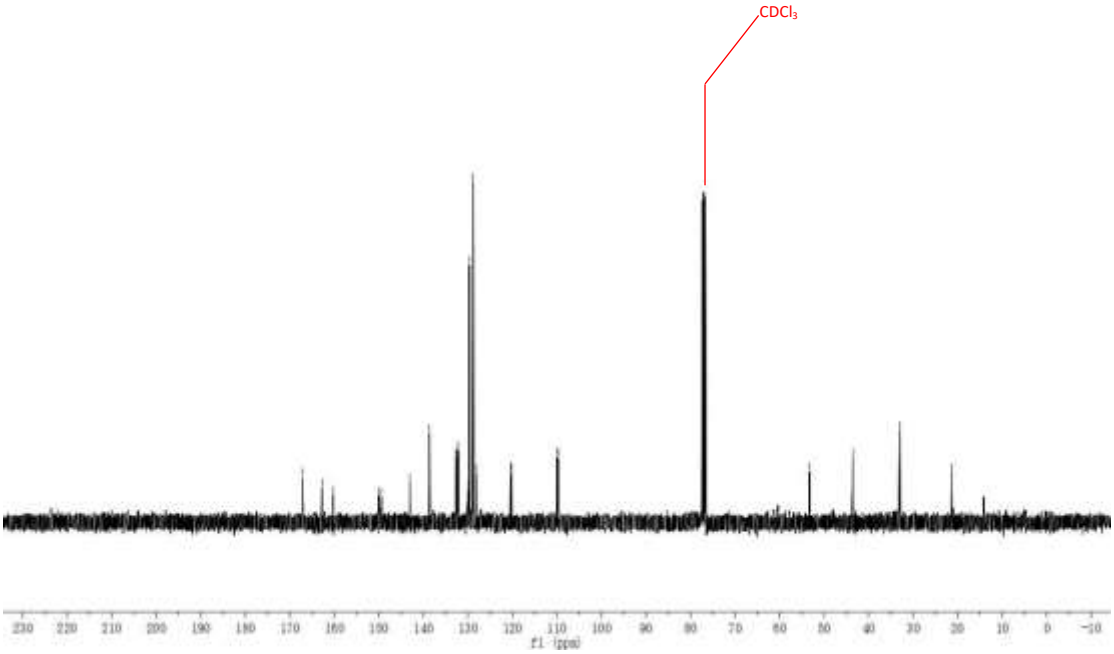


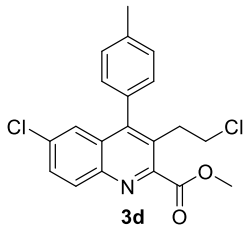
3c

^{1}H NMR (400 MHz)

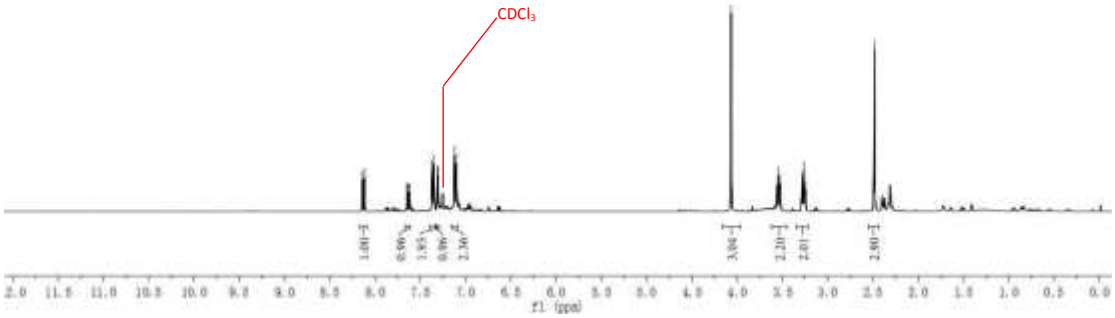


^{13}C NMR (101 MHz)

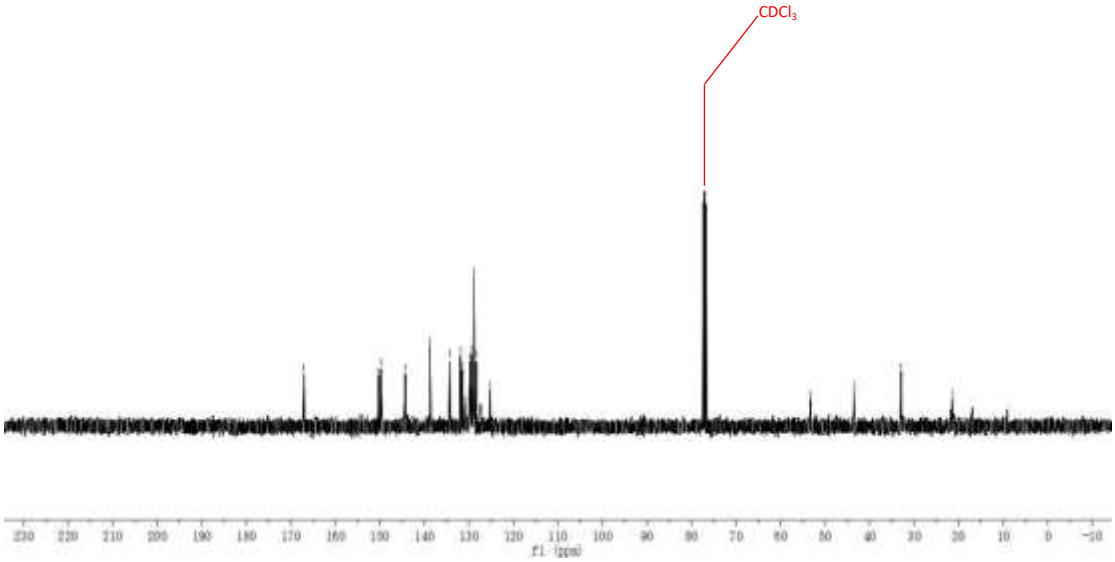


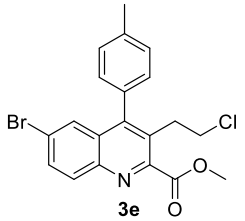


^{1}H NMR (400 MHz)

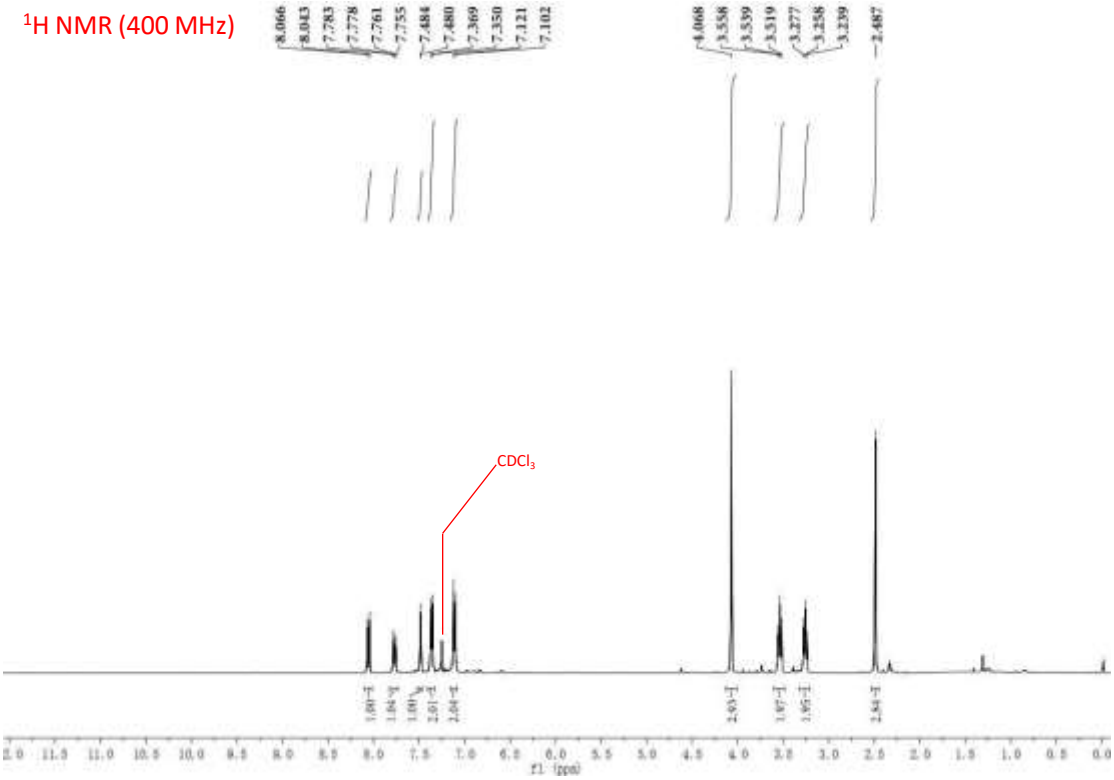


^{13}C NMR (101 MHz)

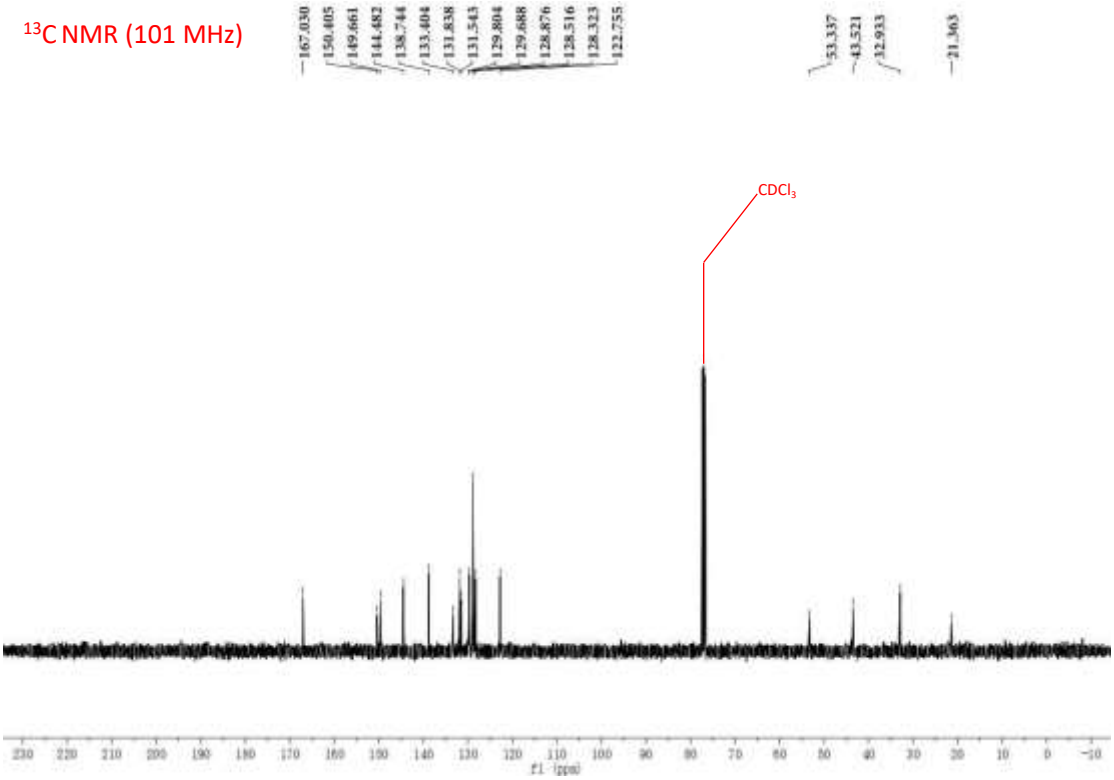


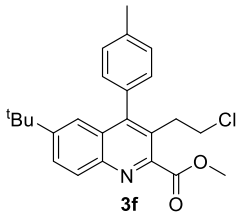


^{1}H NMR (400 MHz)

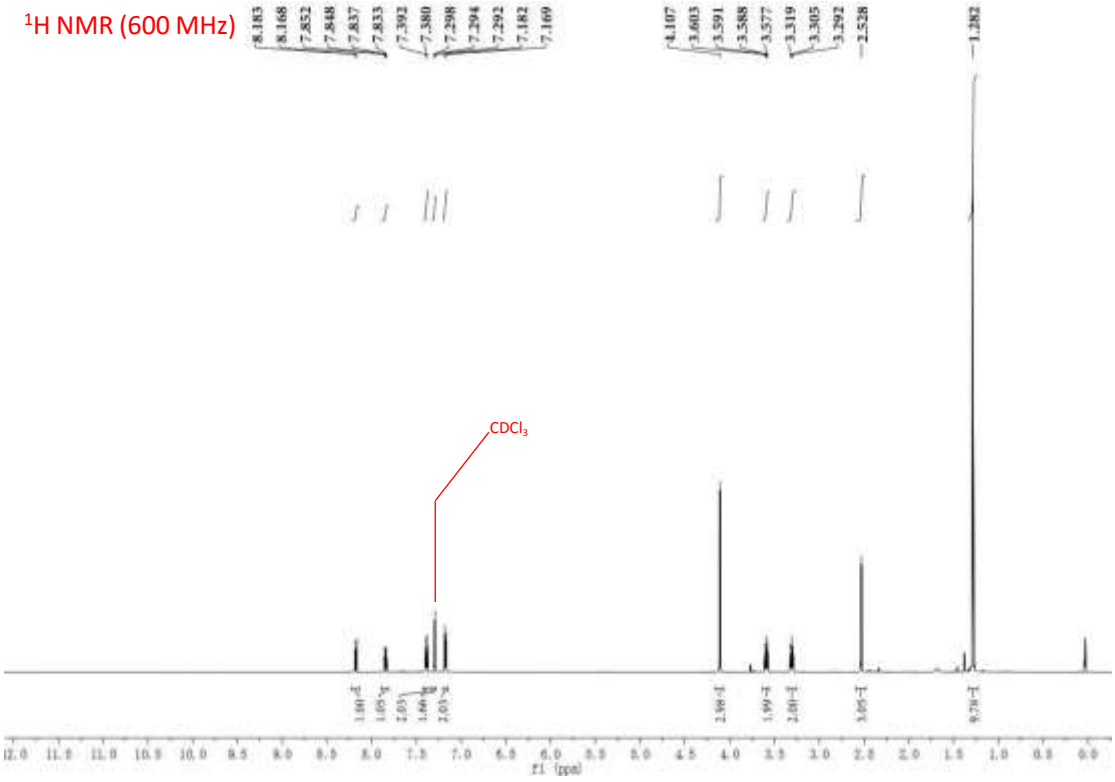


^{13}C NMR (101 MHz)

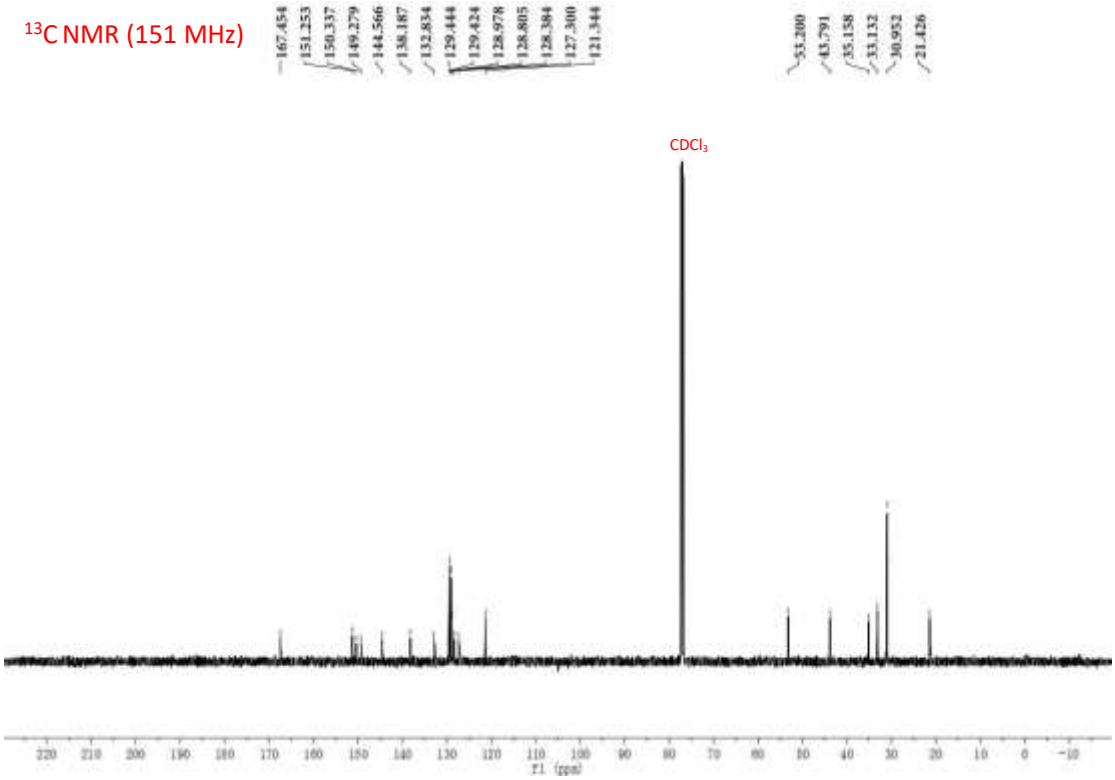


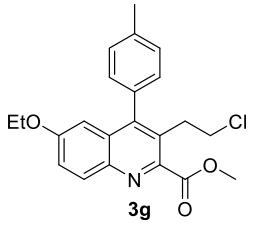


^{1}H NMR (600 MHz)

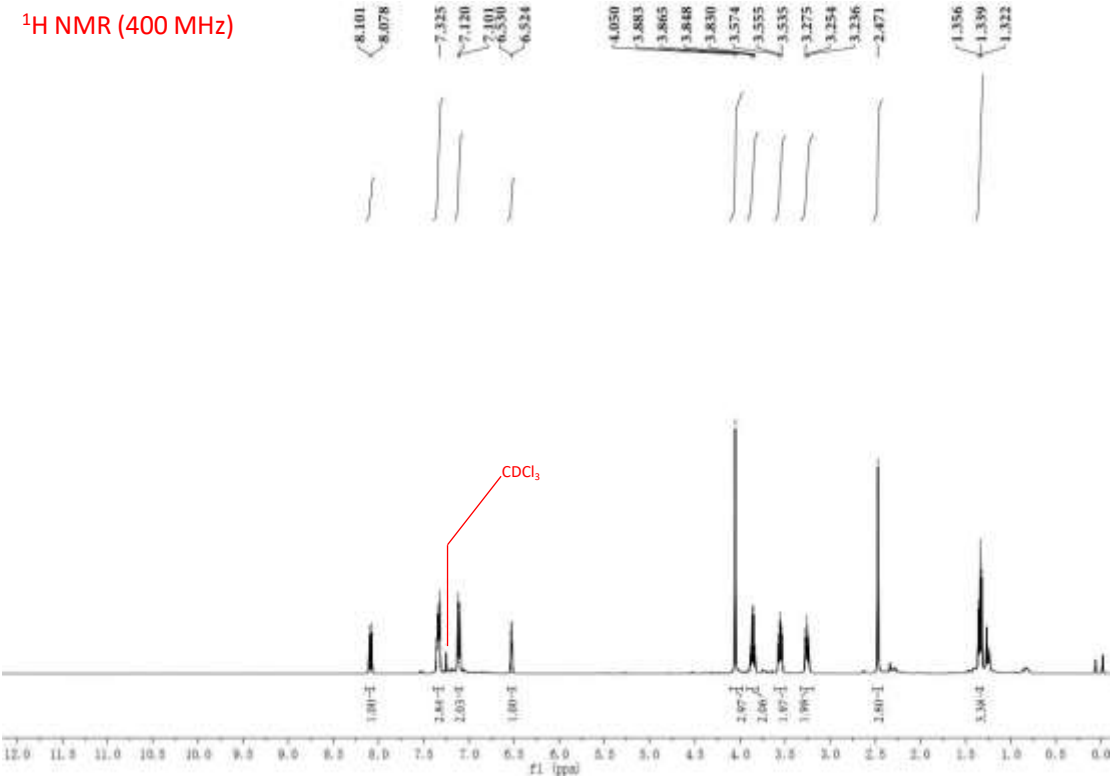


^{13}C NMR (151 MHz)

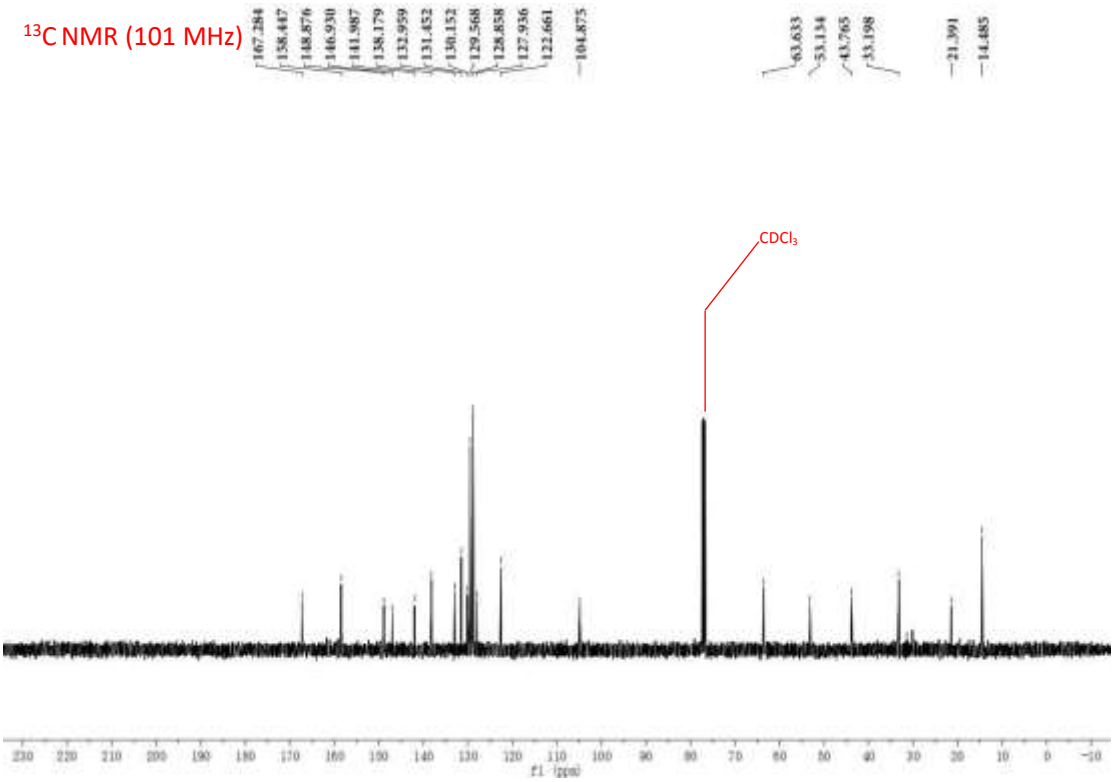


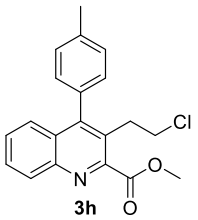


^{1}H NMR (400 MHz)



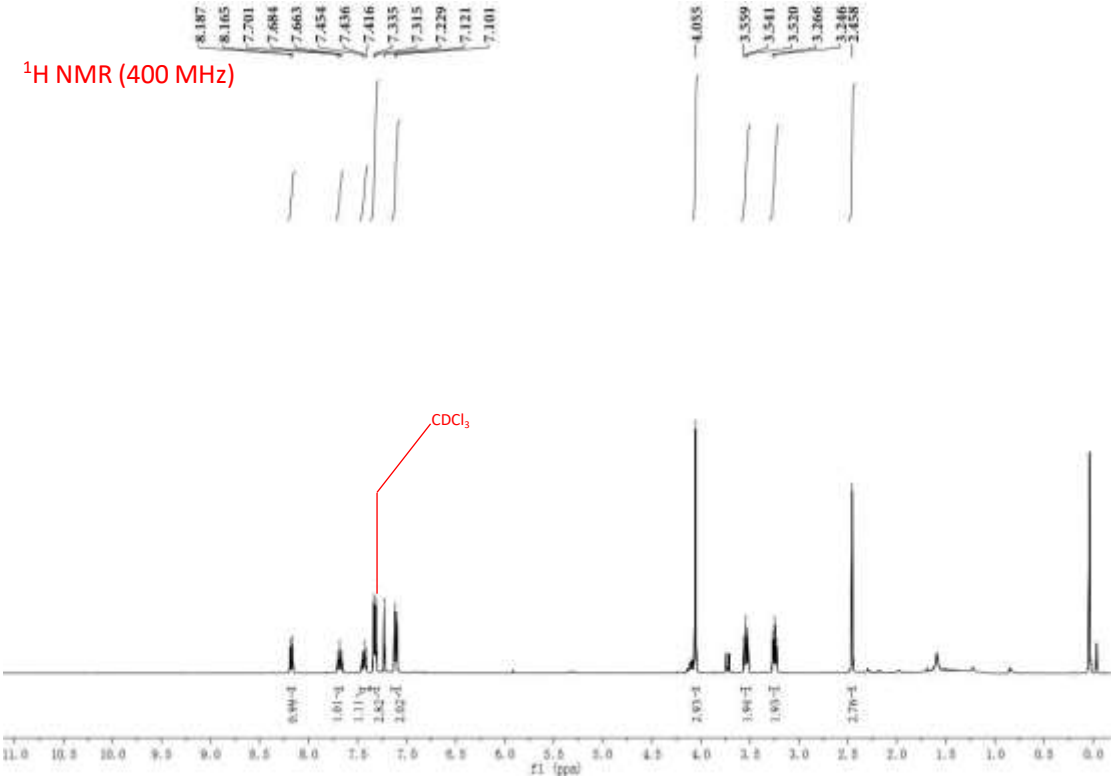
^{13}C NMR (101 MHz)



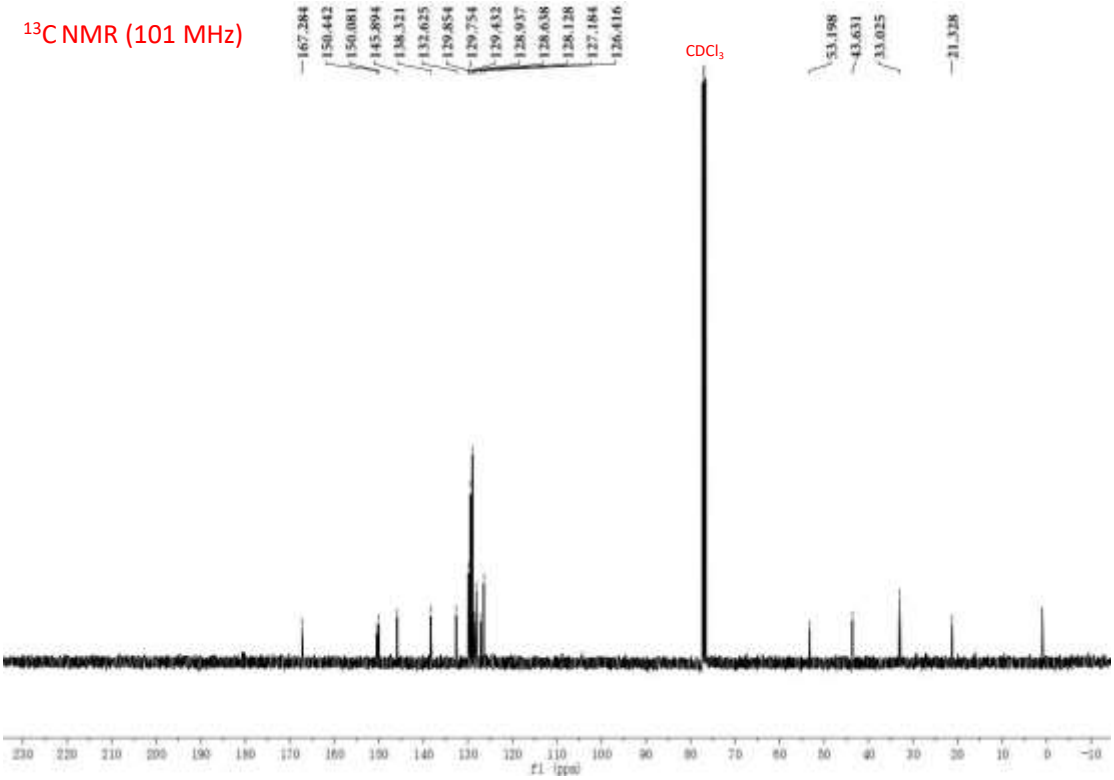


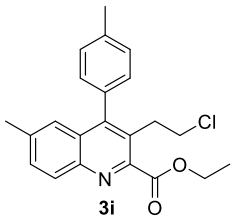
3h

^{1}H NMR (400 MHz)



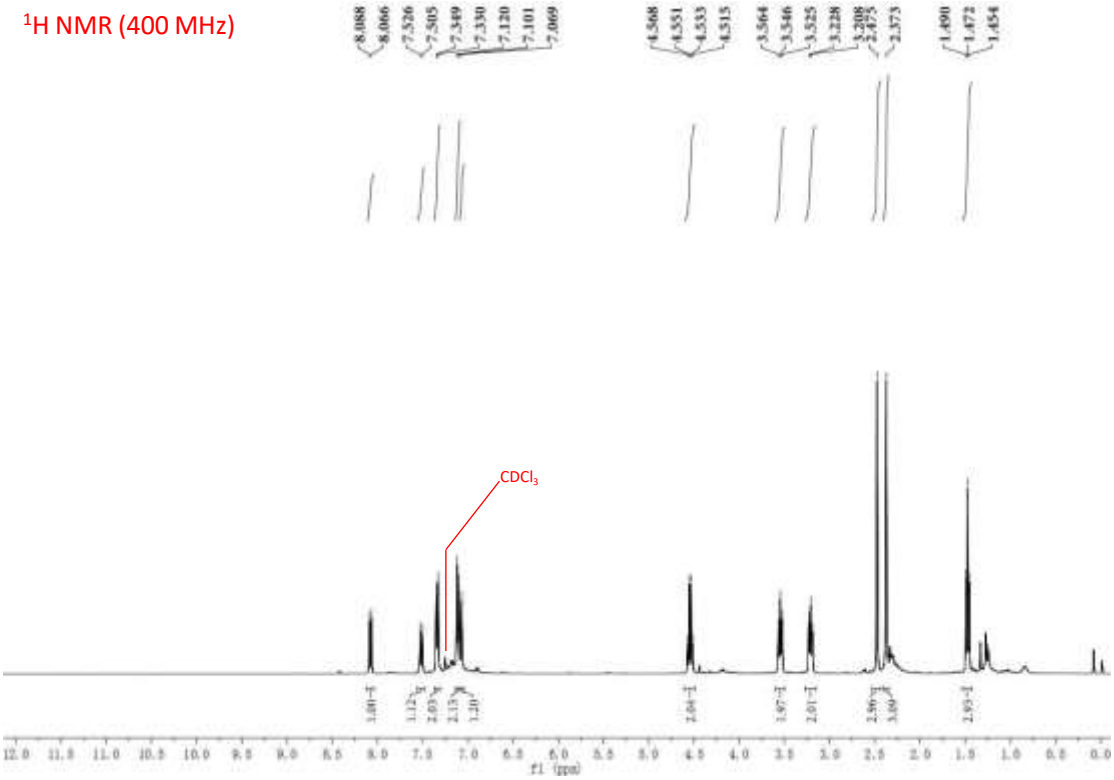
^{13}C NMR (101 MHz)



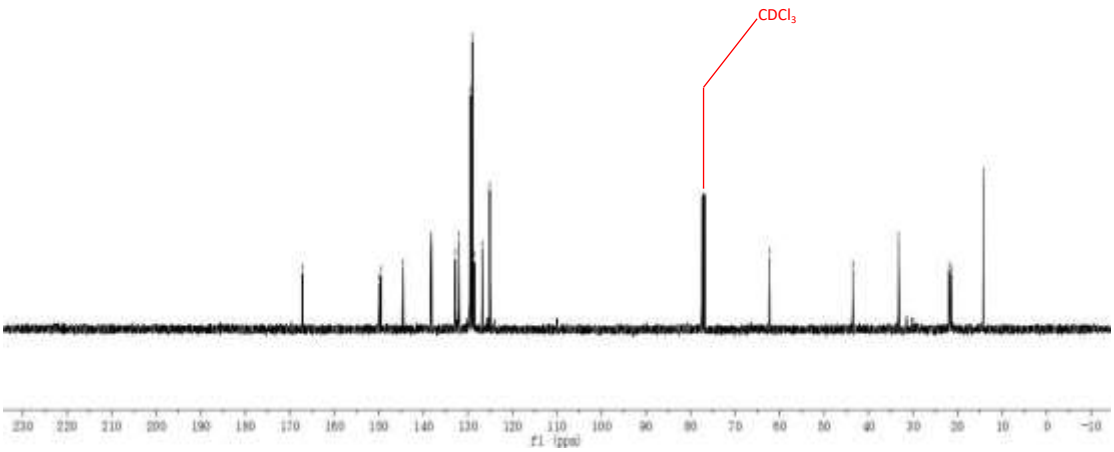


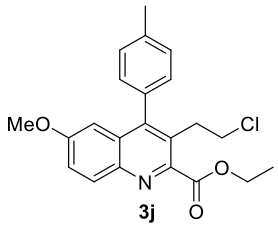
3i

^{1}H NMR (400 MHz)

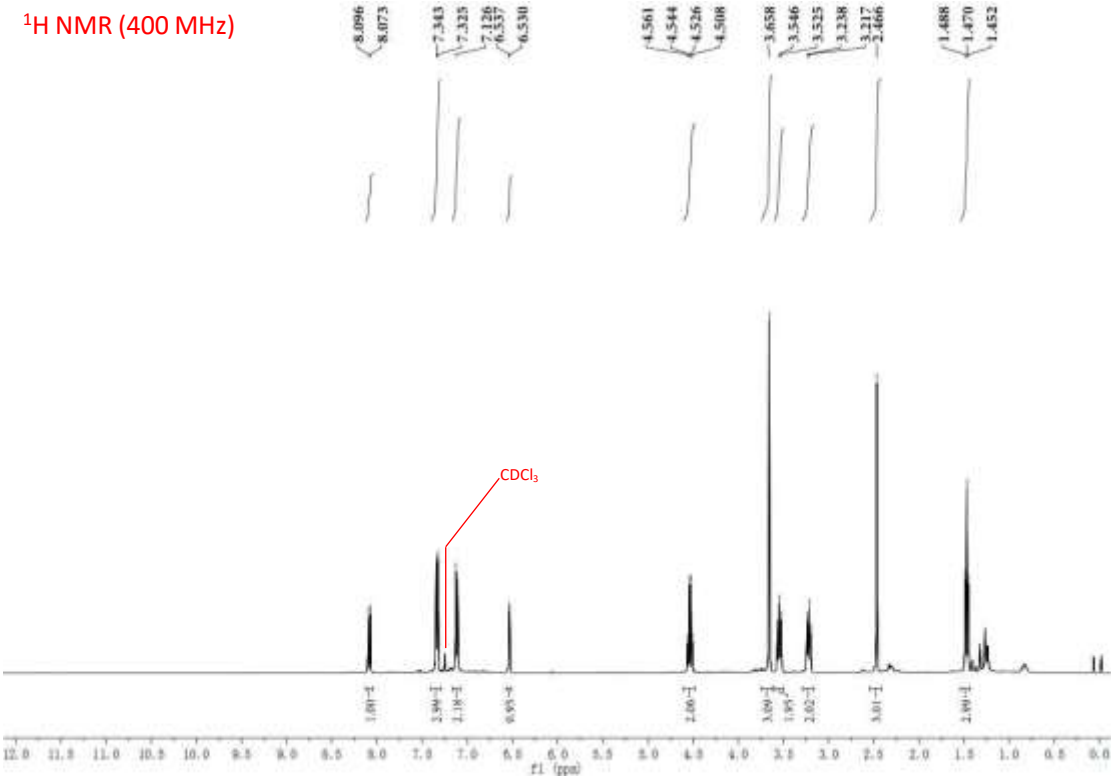


^{13}C NMR (101 MHz)

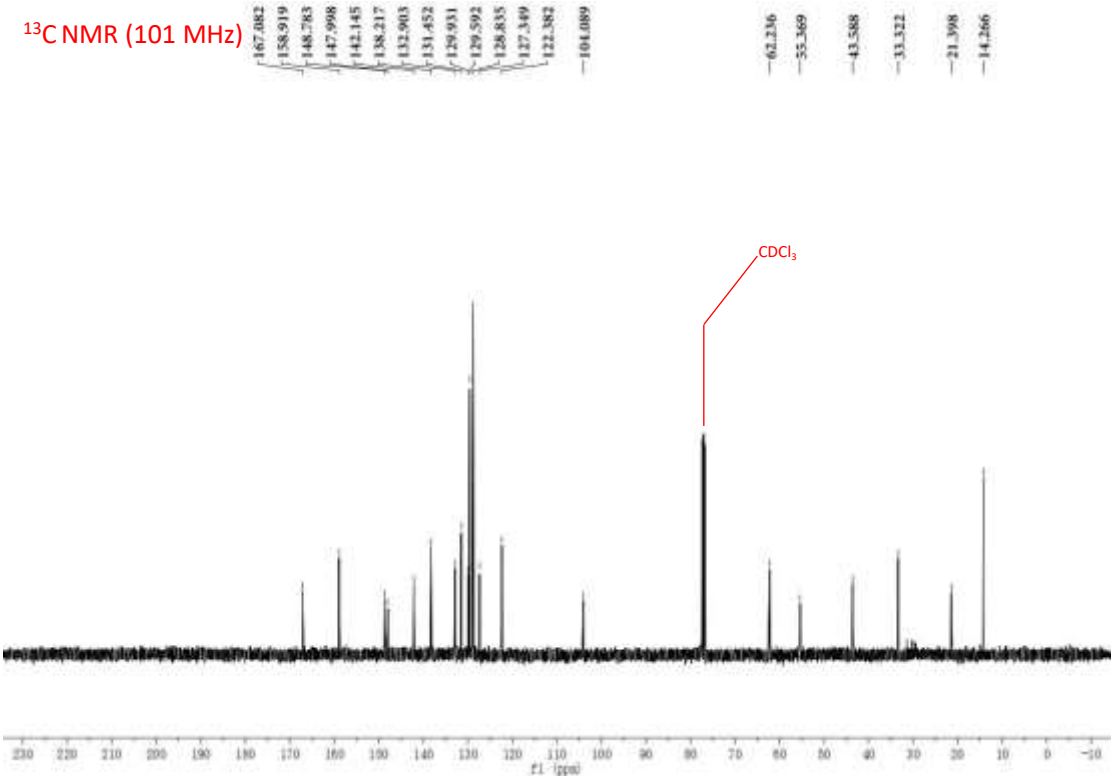


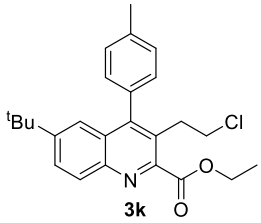


^{1}H NMR (400 MHz)

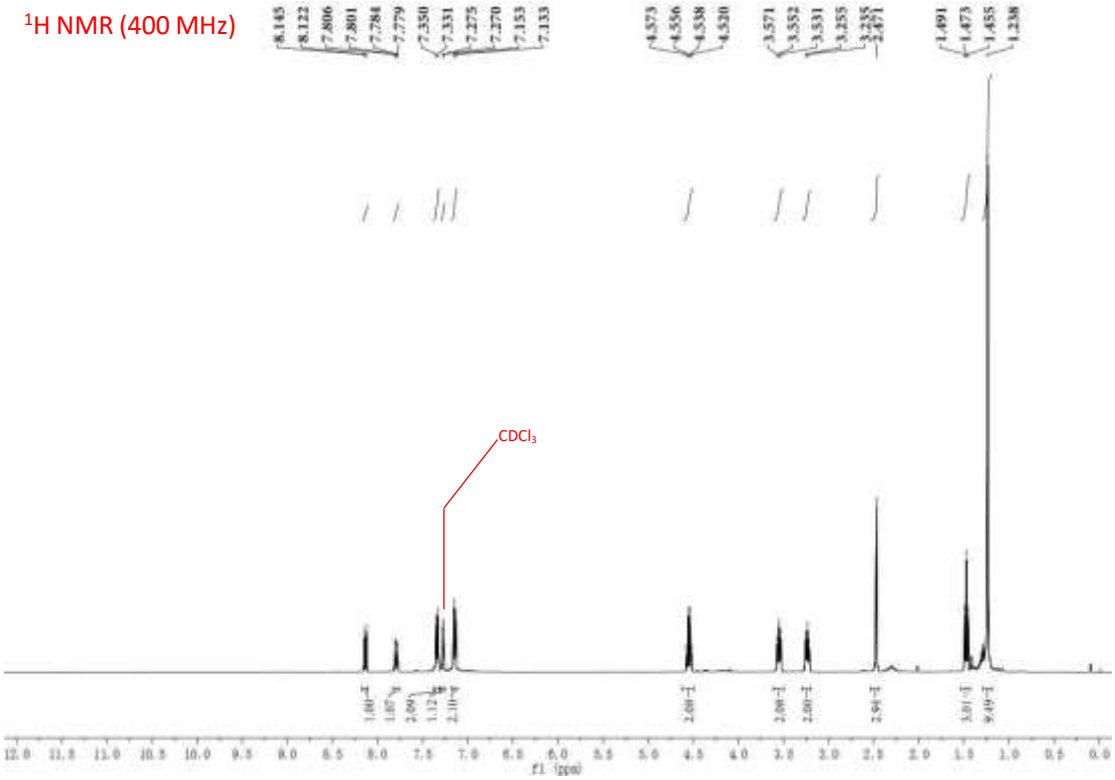


^{13}C NMR (101 MHz)

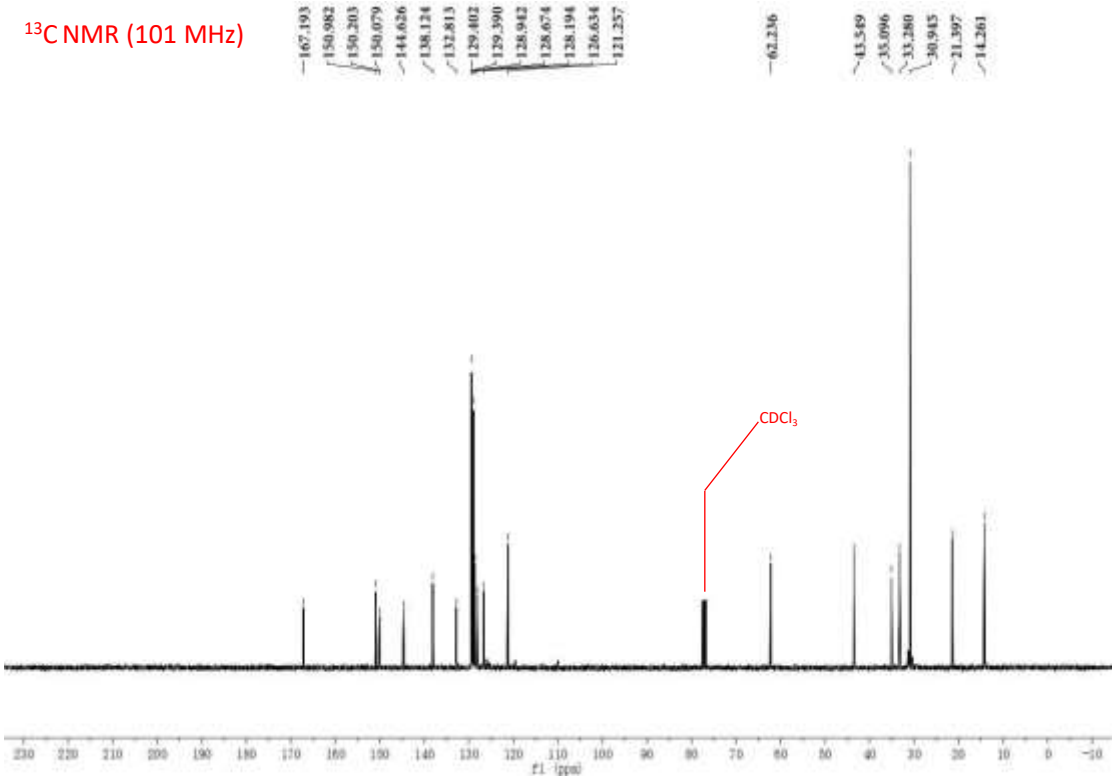


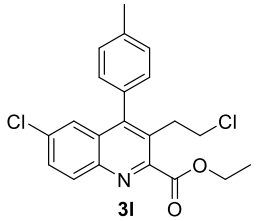


^{1}H NMR (400 MHz)

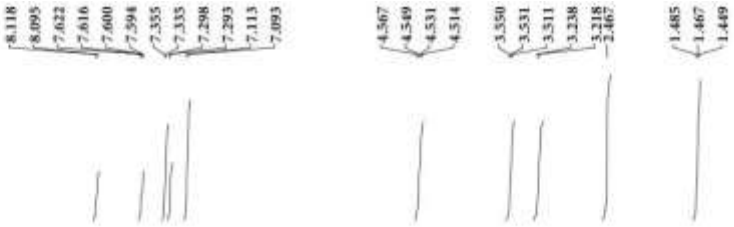


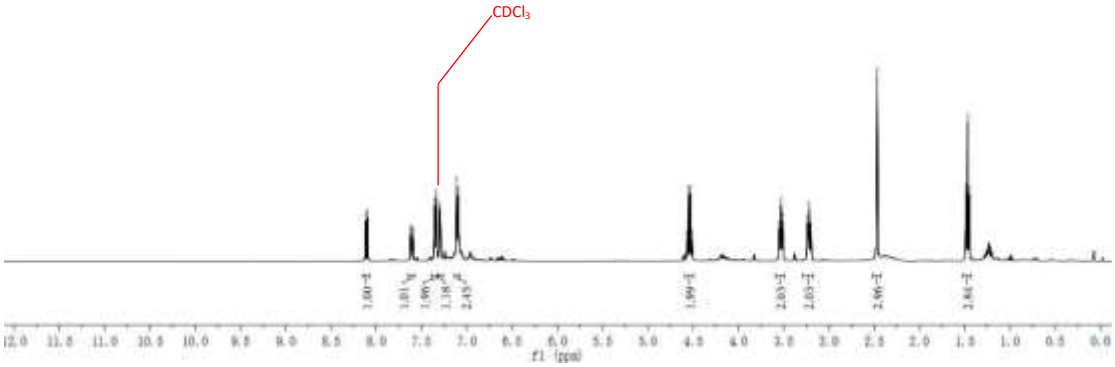
^{13}C NMR (101 MHz)



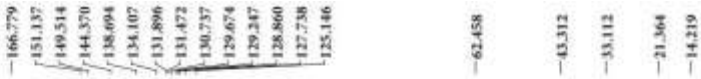


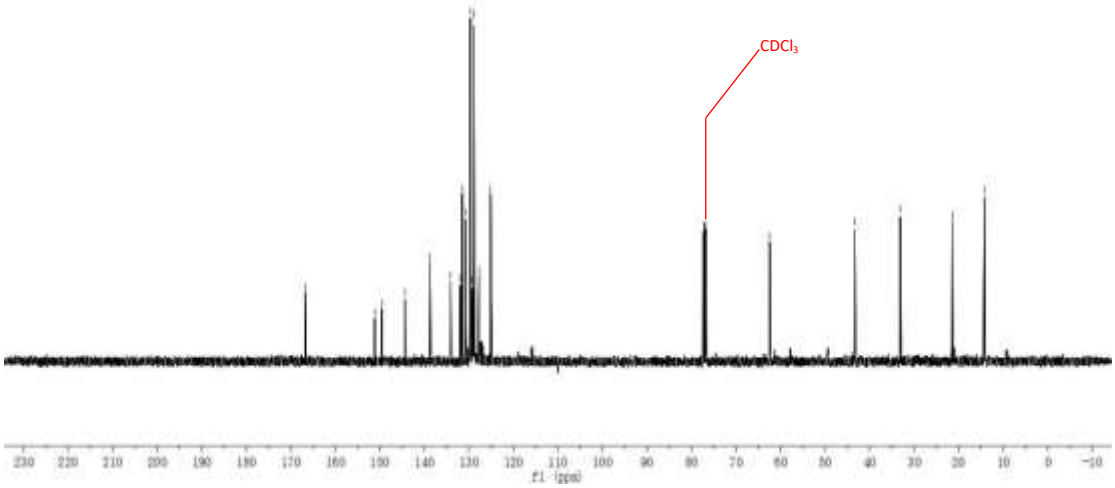
^{1}H NMR (400 MHz)

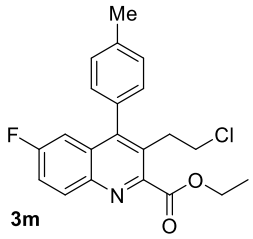




^{13}C NMR (101 MHz)

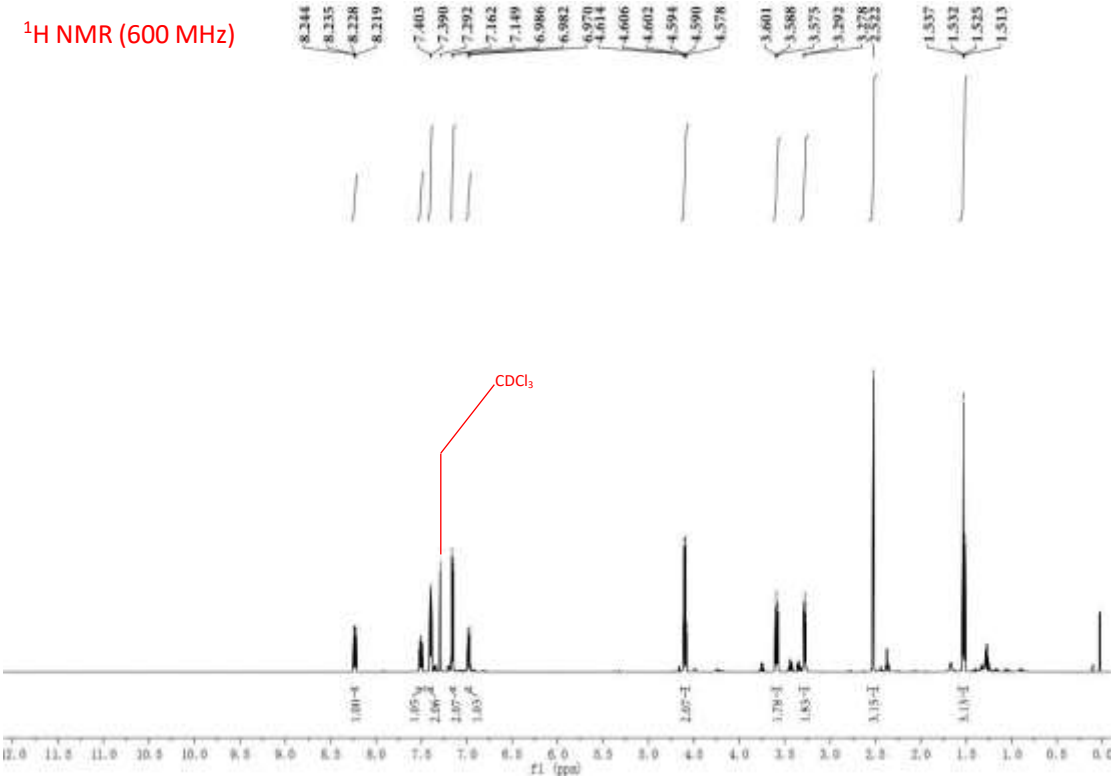




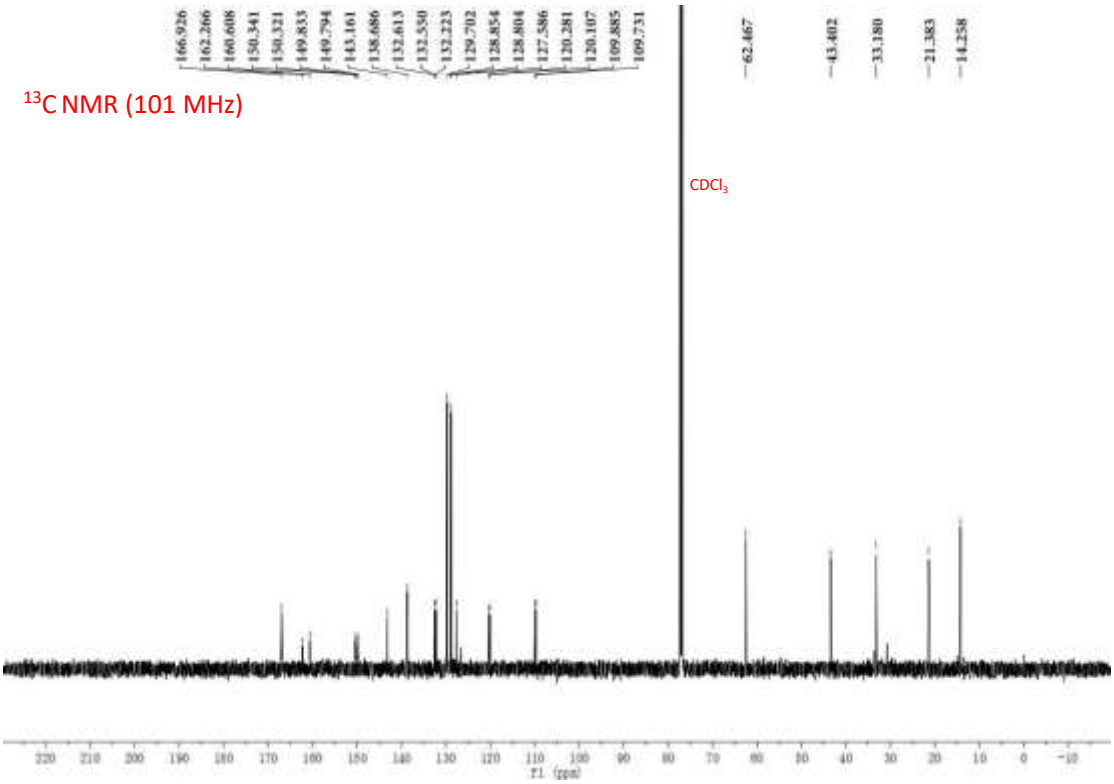


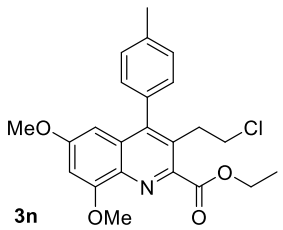
3m

^{1}H NMR (600 MHz)



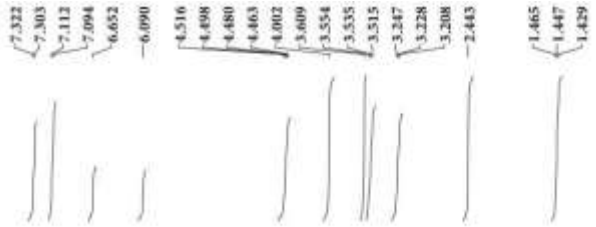
^{13}C NMR (101 MHz)

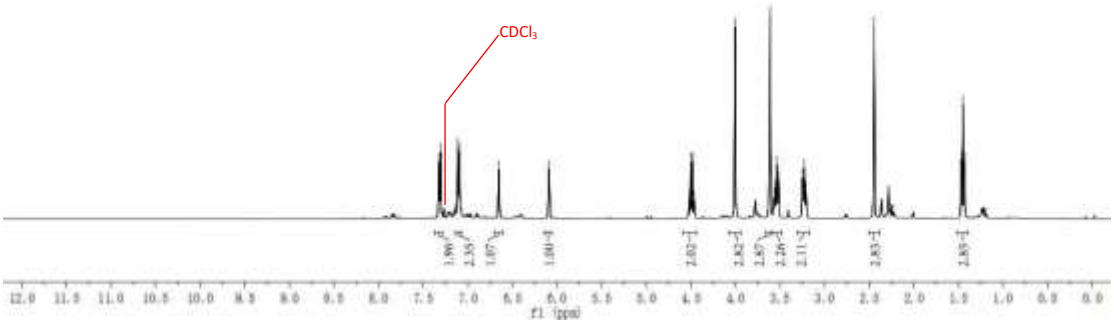




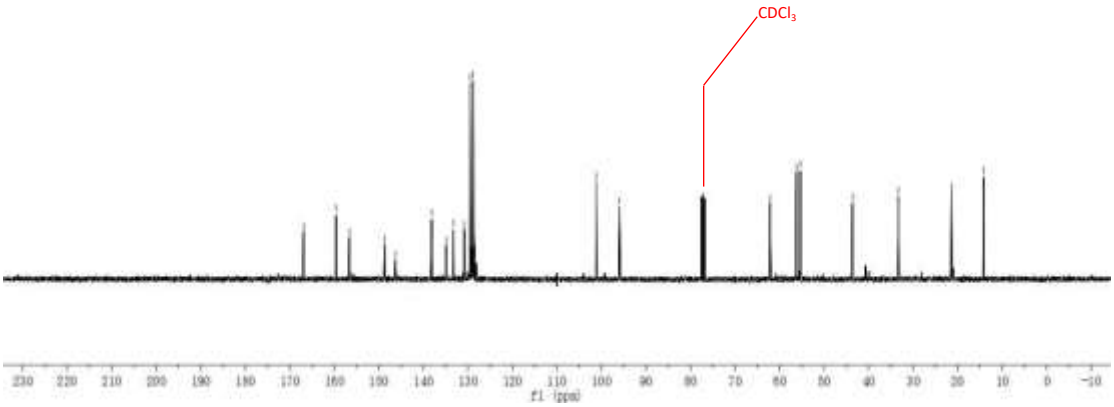
3n

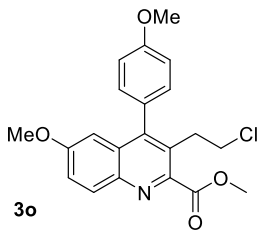
^{1}H NMR (400 MHz)





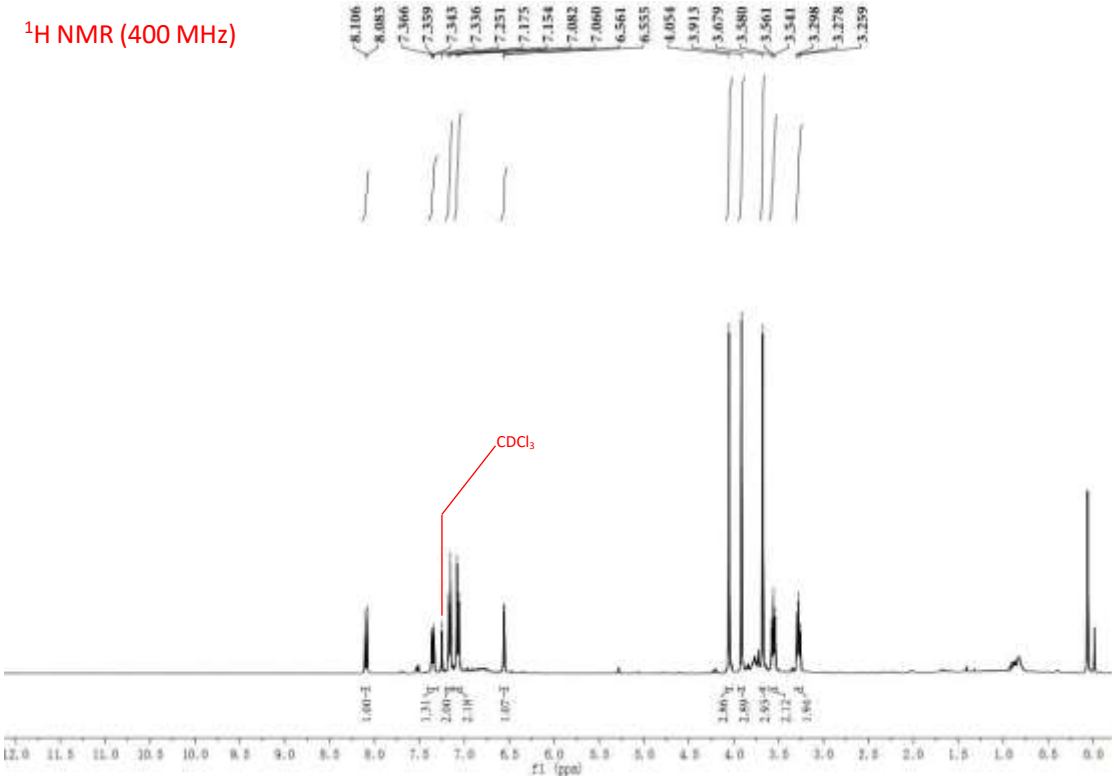
^{13}C NMR (101 MHz)



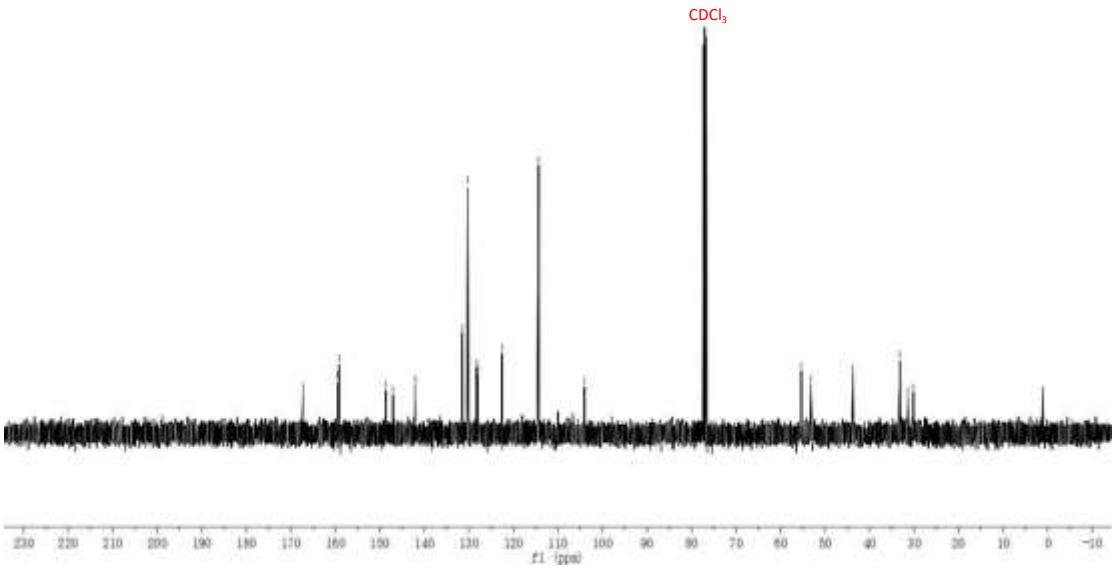


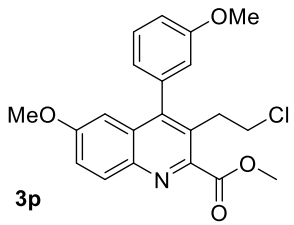
3o

^{1}H NMR (400 MHz)



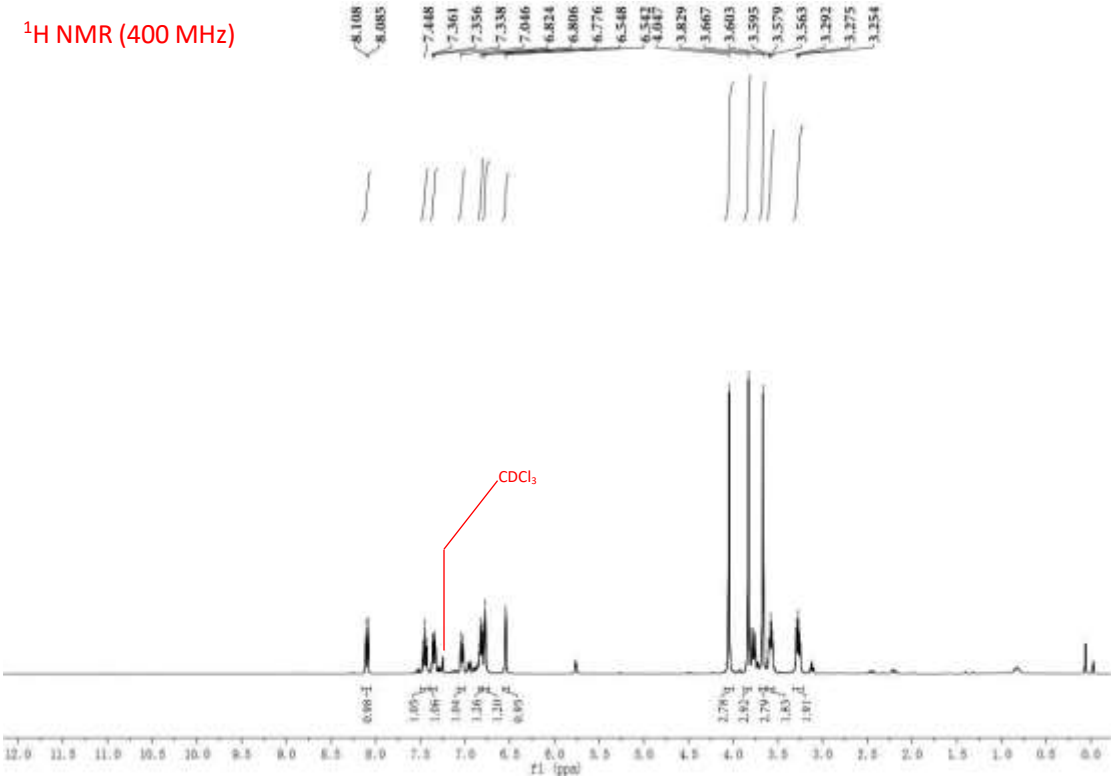
^{13}C NMR (101 MHz)



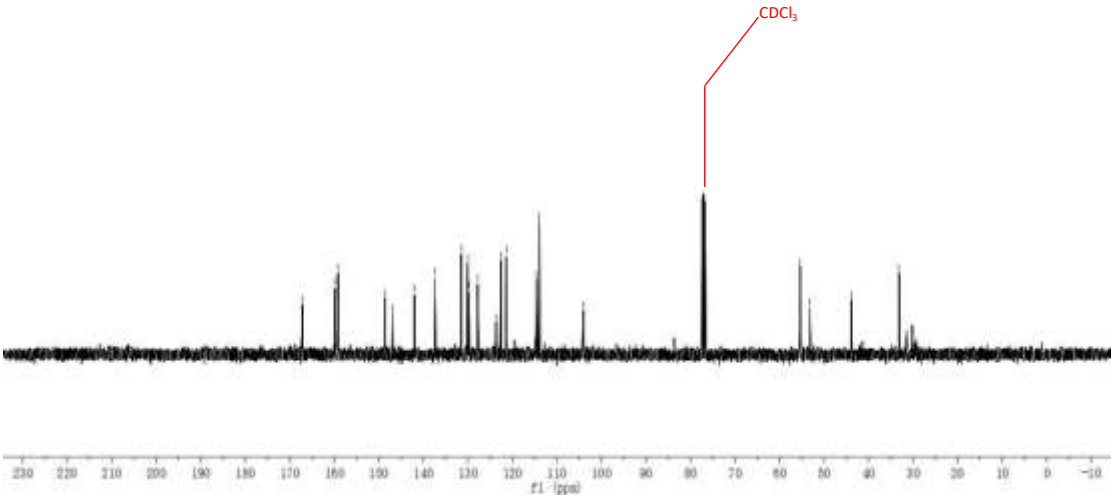


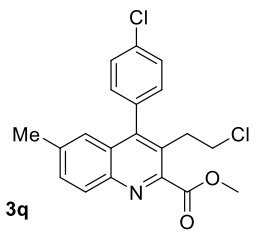
3p

^{1}H NMR (400 MHz)



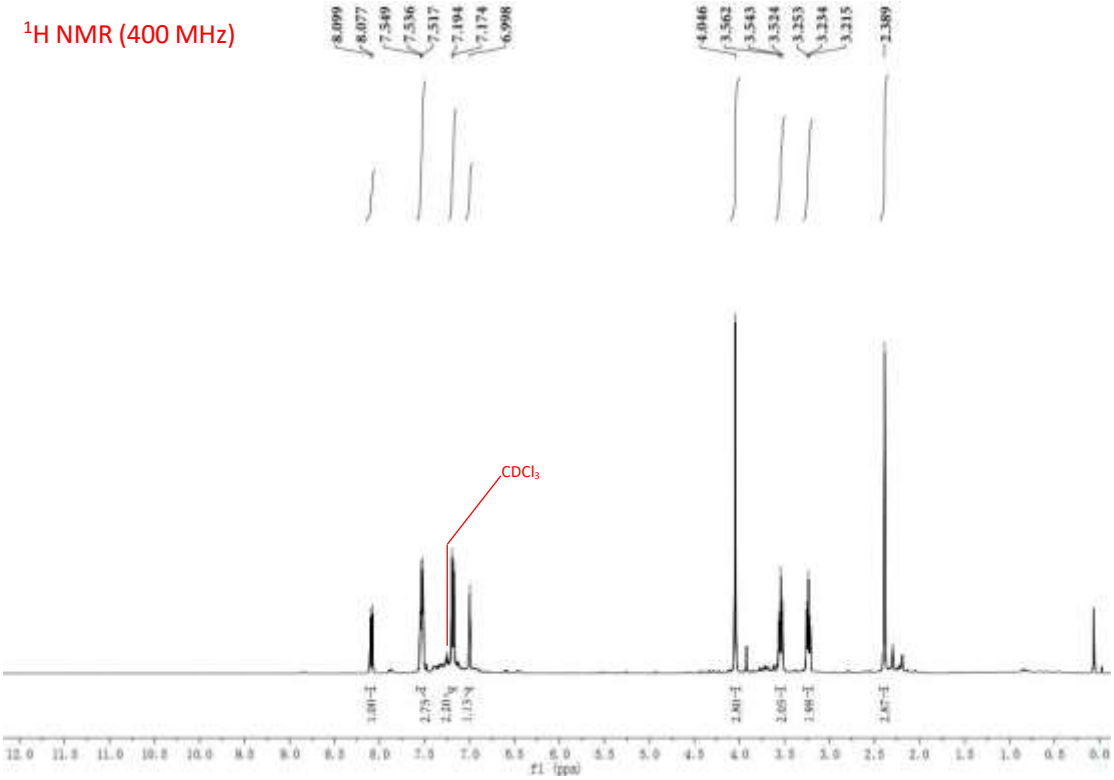
^{13}C NMR (101 MHz)



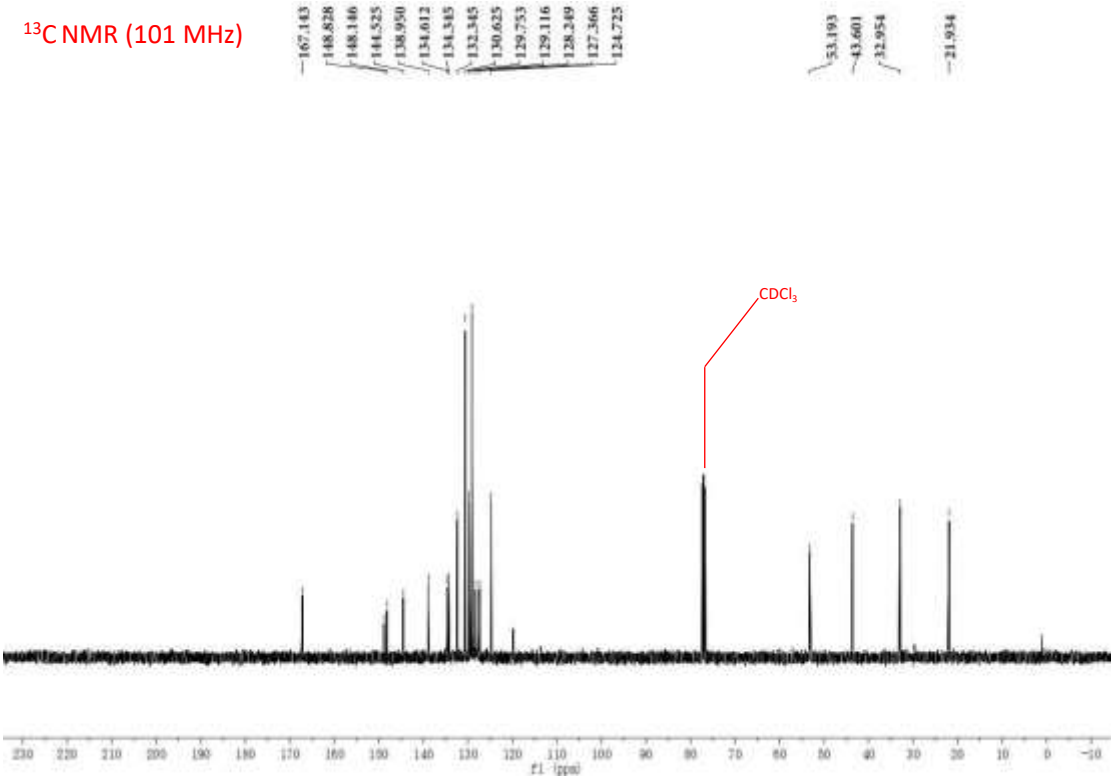


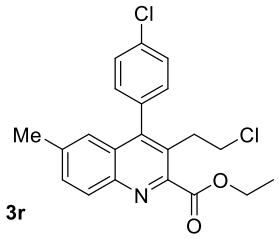
3q

^{1}H NMR (400 MHz)



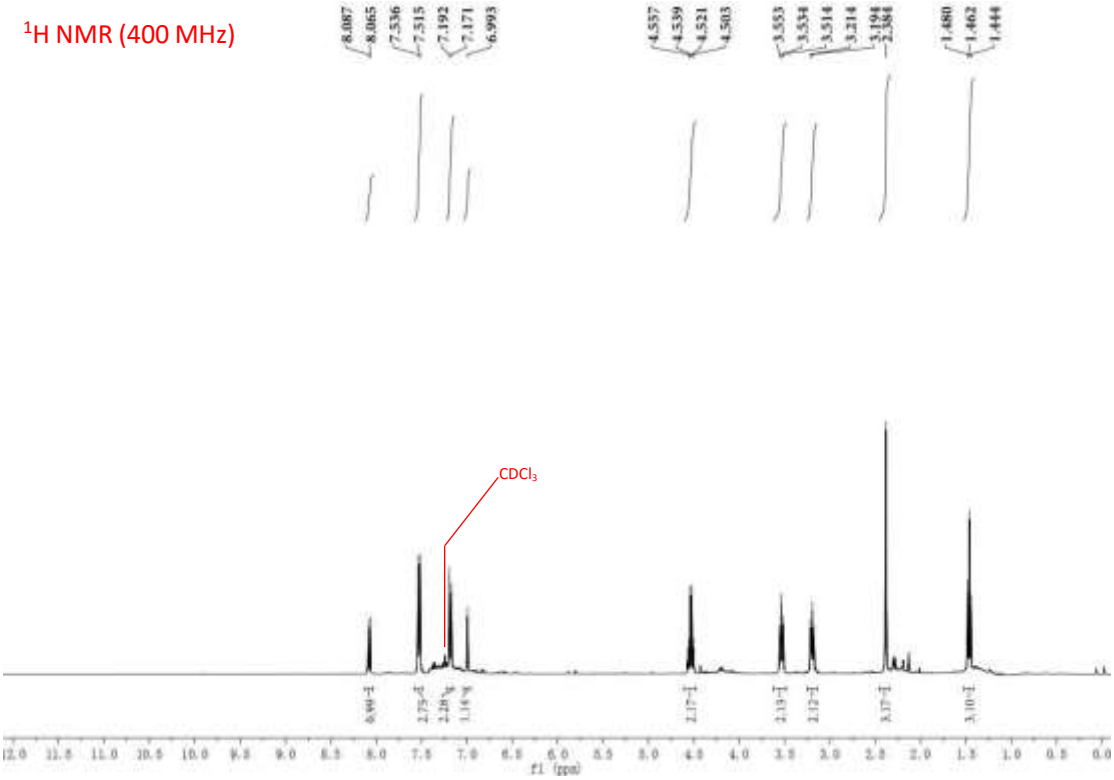
^{13}C NMR (101 MHz)



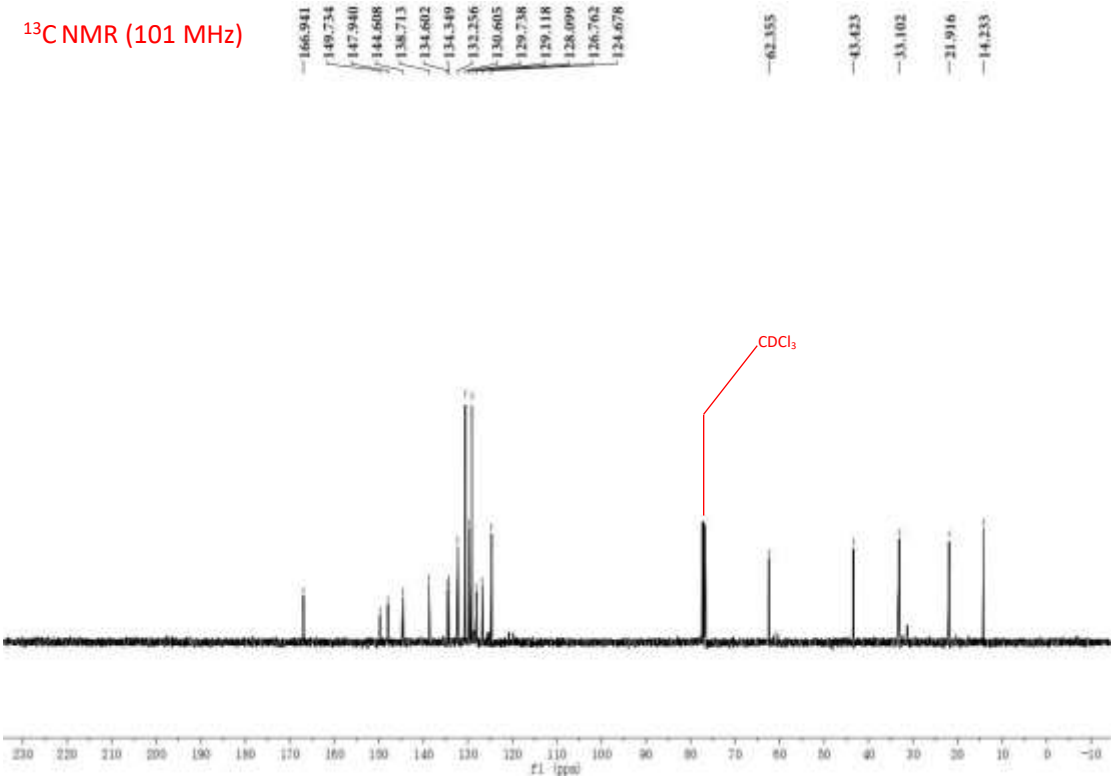


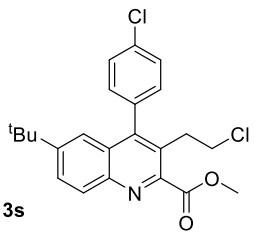
3r

^{1}H NMR (400 MHz)



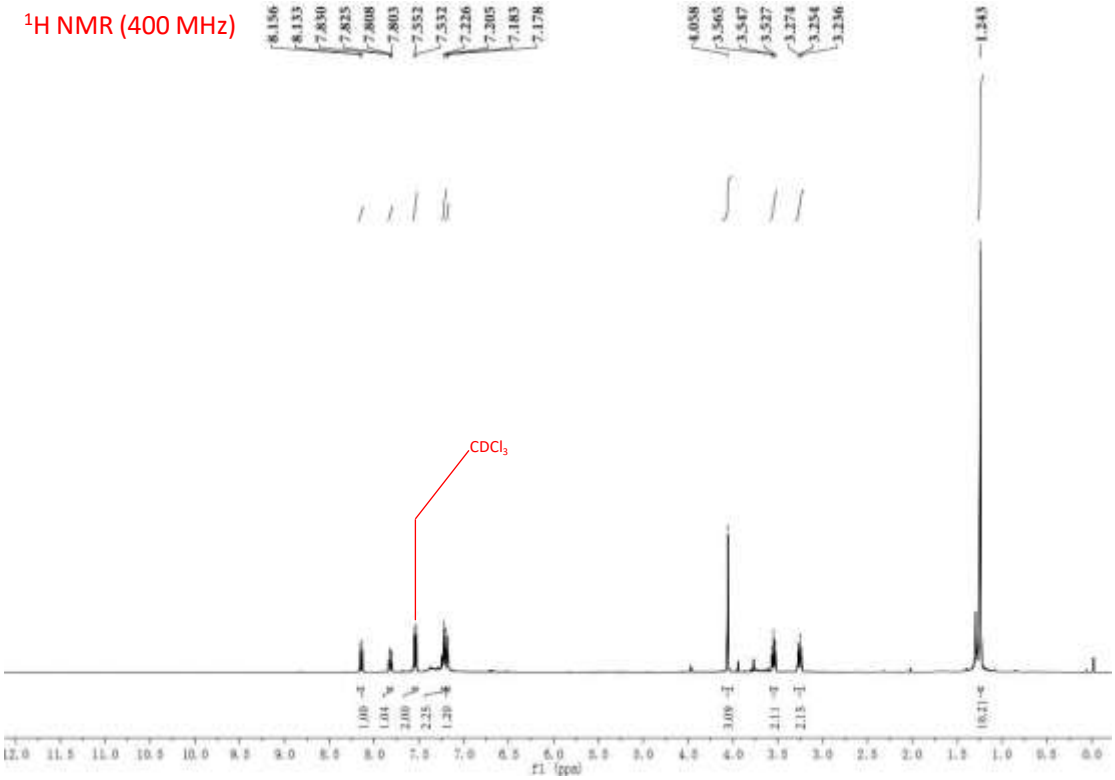
^{13}C NMR (101 MHz)



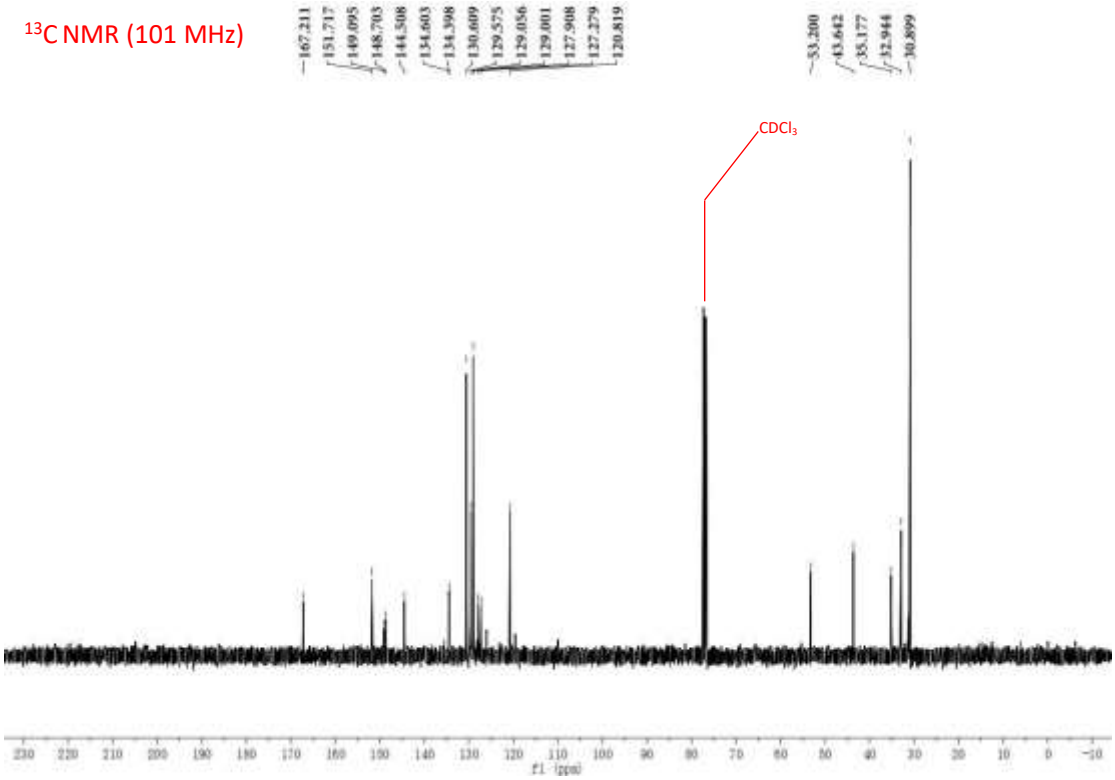


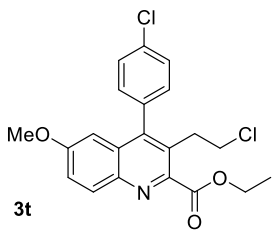
3s

^{1}H NMR (400 MHz)

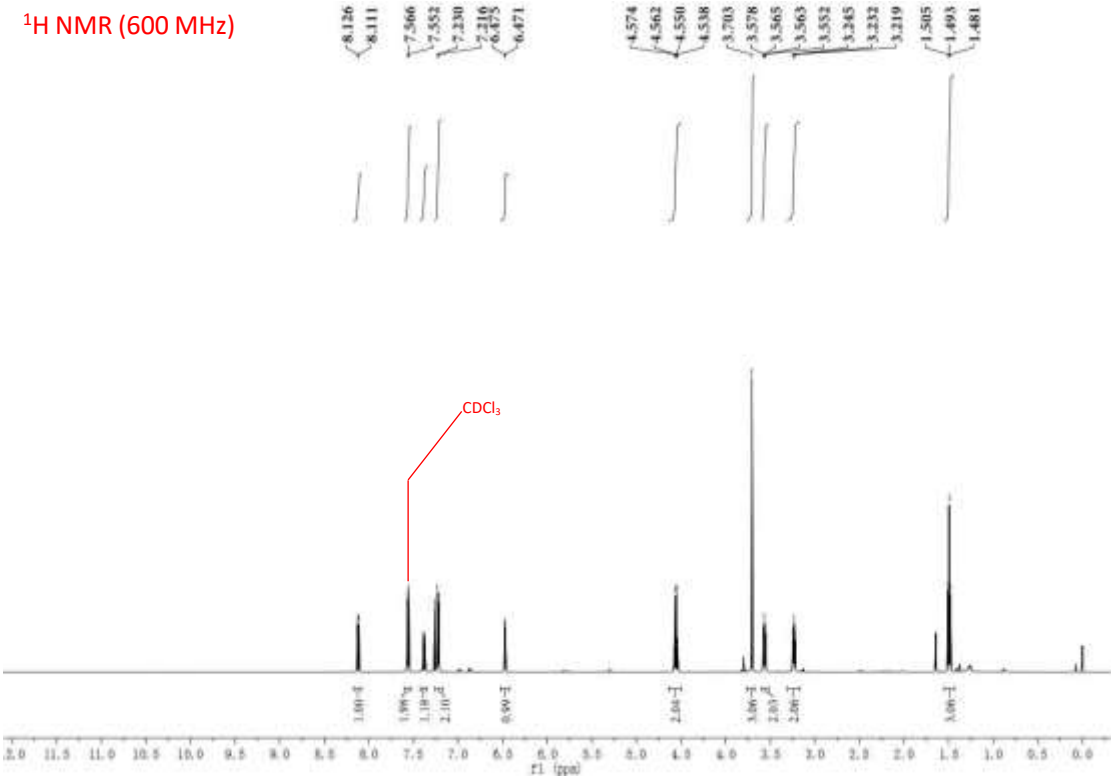


^{13}C NMR (101 MHz)

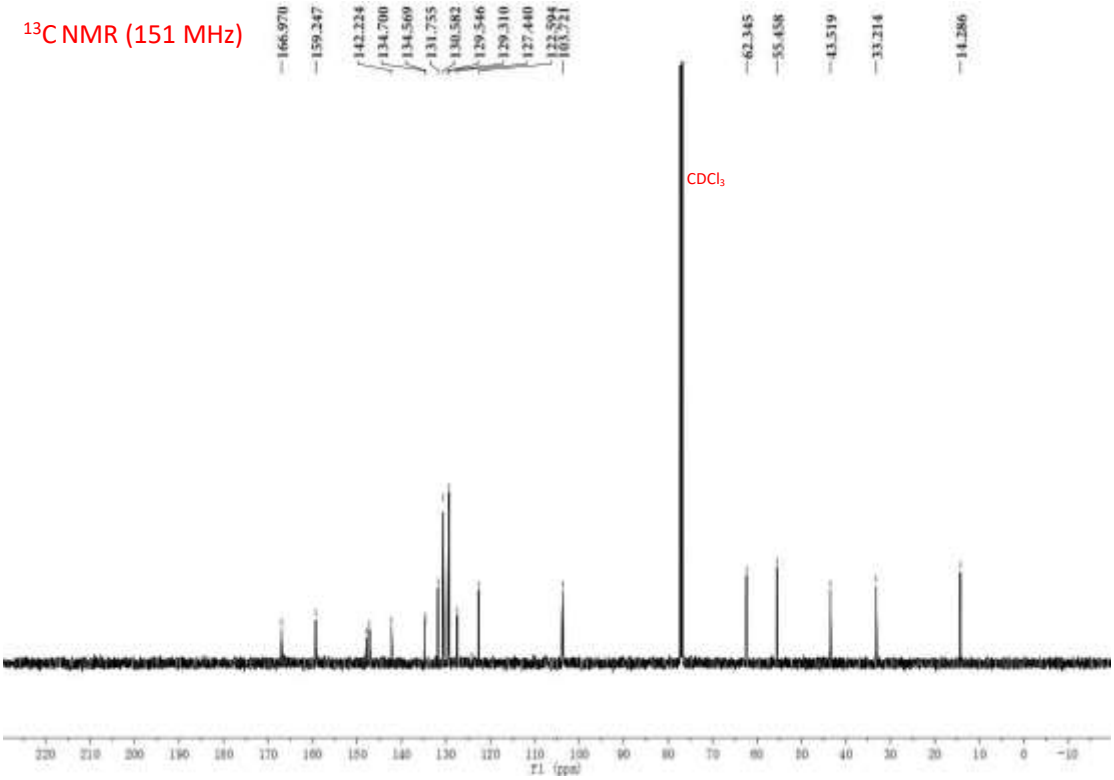


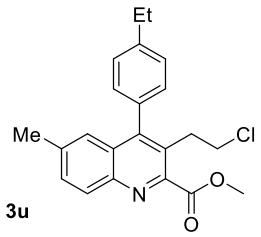


^{1}H NMR (600 MHz)



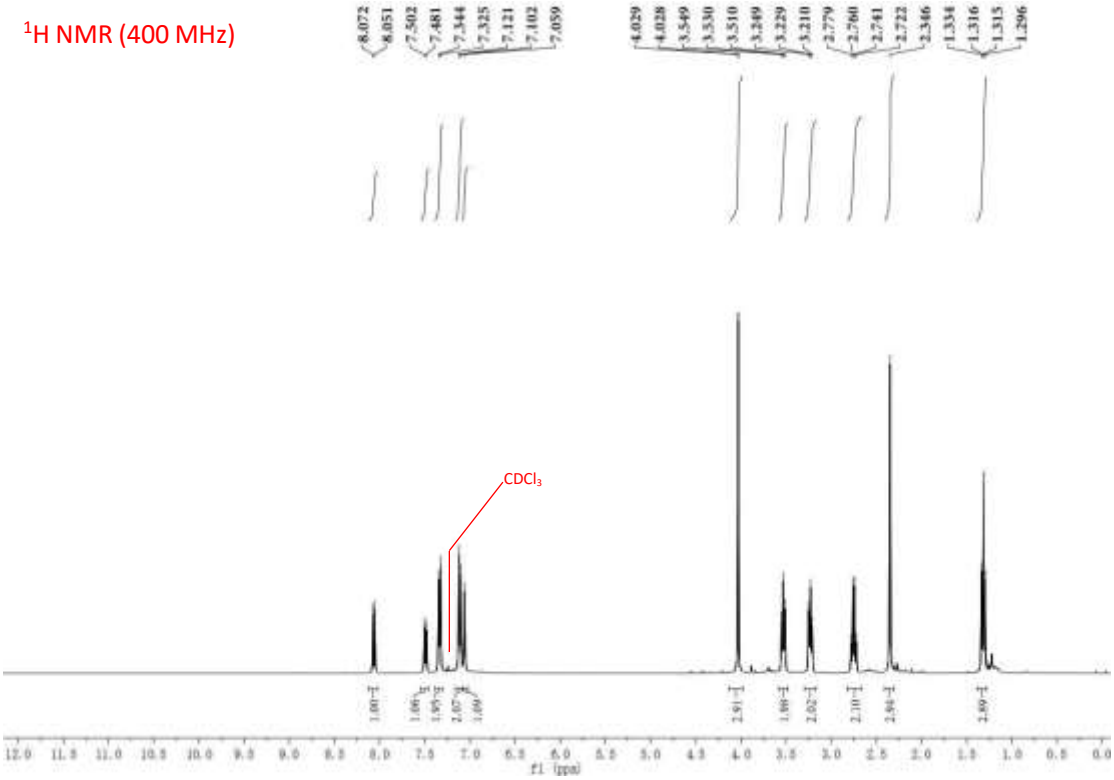
^{13}C NMR (151 MHz)



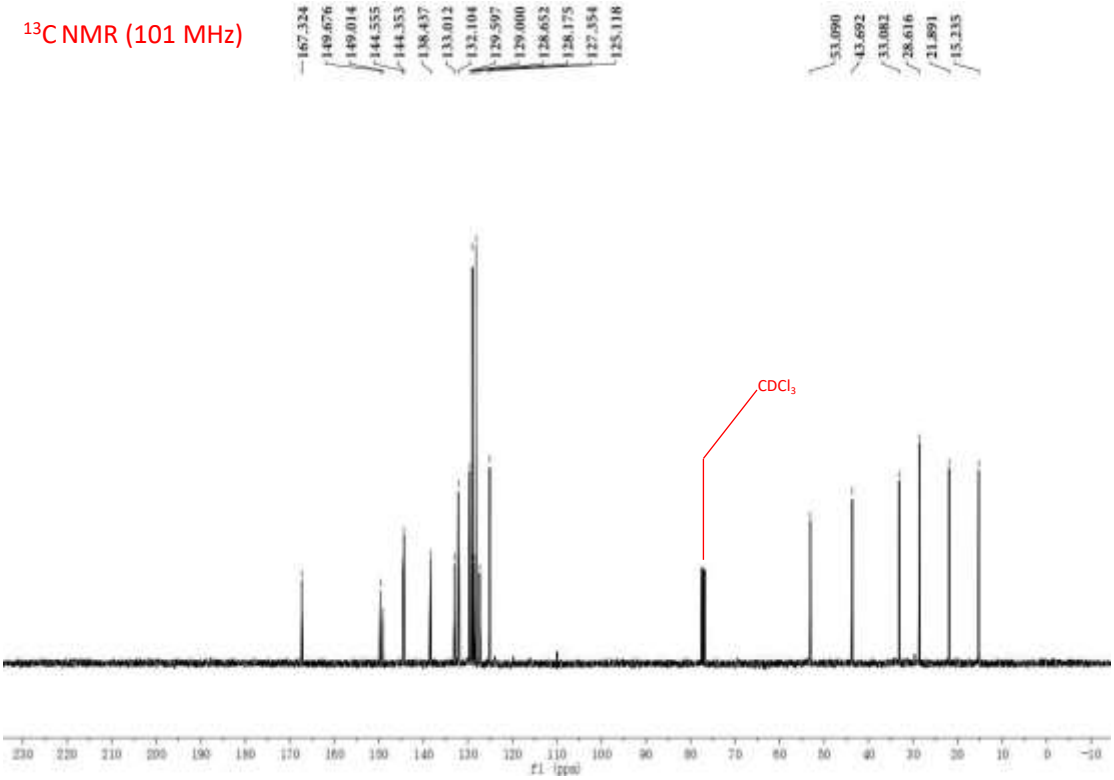


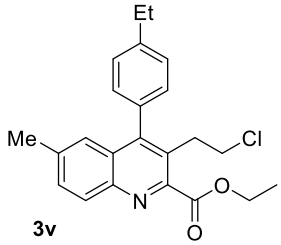
3u

^{1}H NMR (400 MHz)



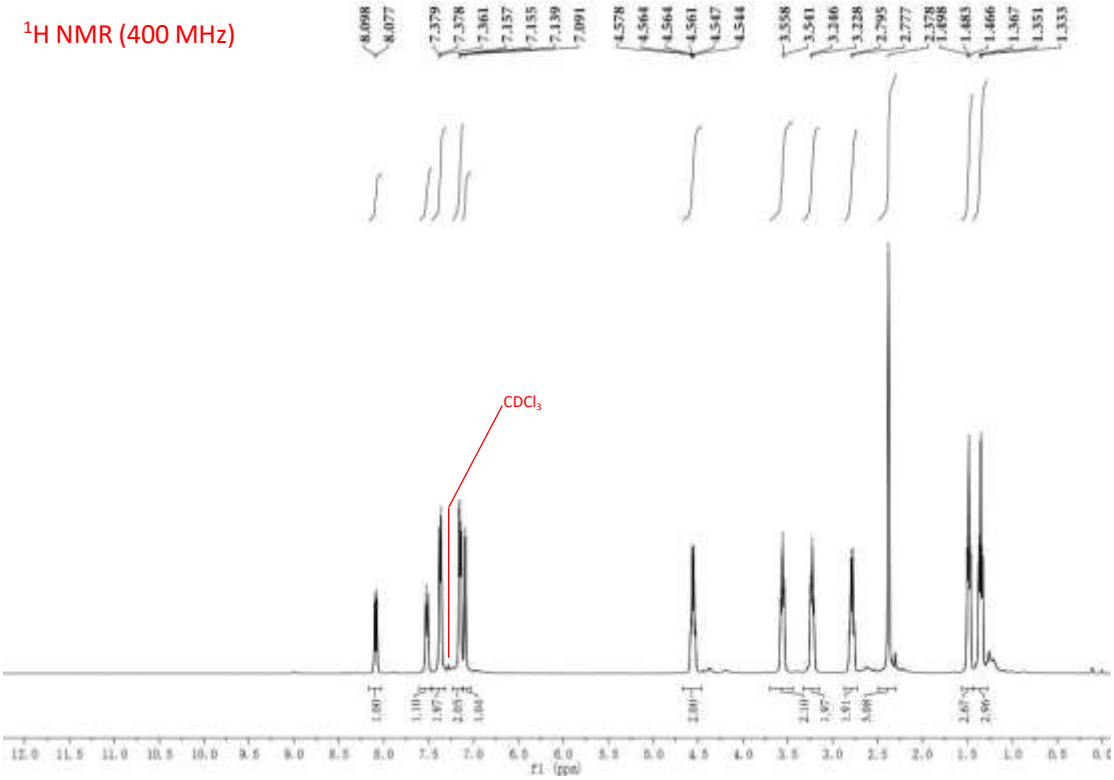
^{13}C NMR (101 MHz)



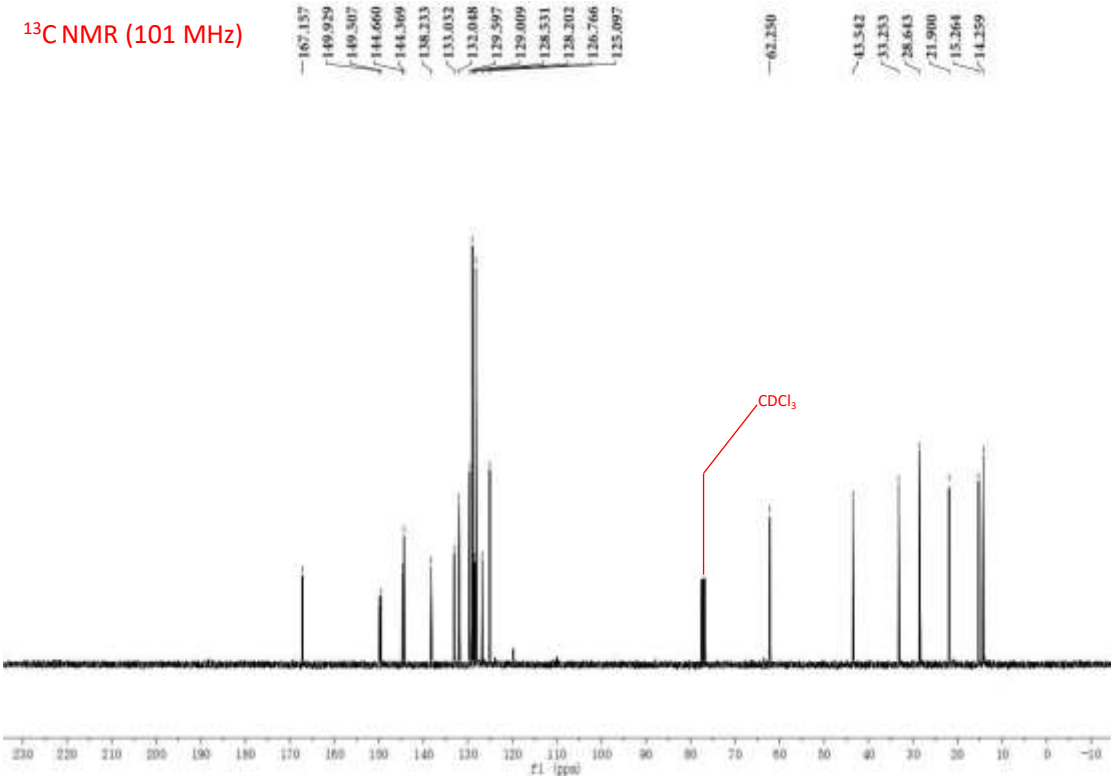


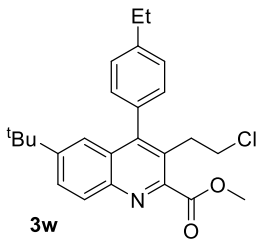
3v

^{1}H NMR (400 MHz)

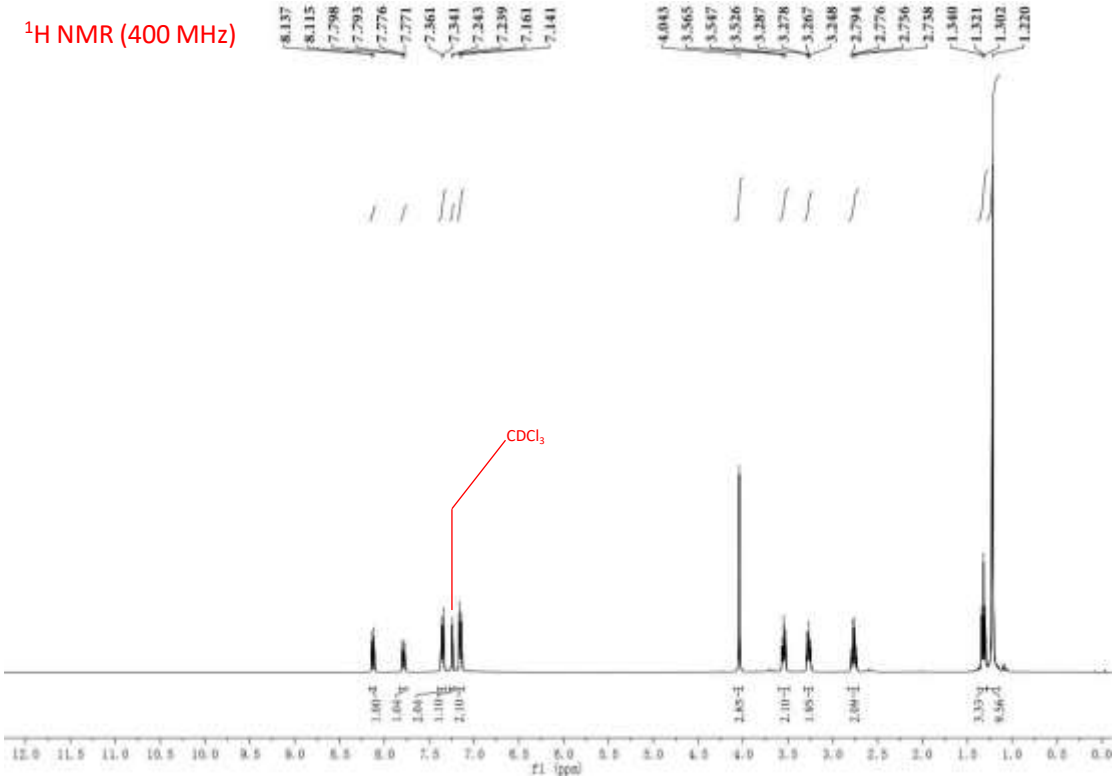


^{13}C NMR (101 MHz)

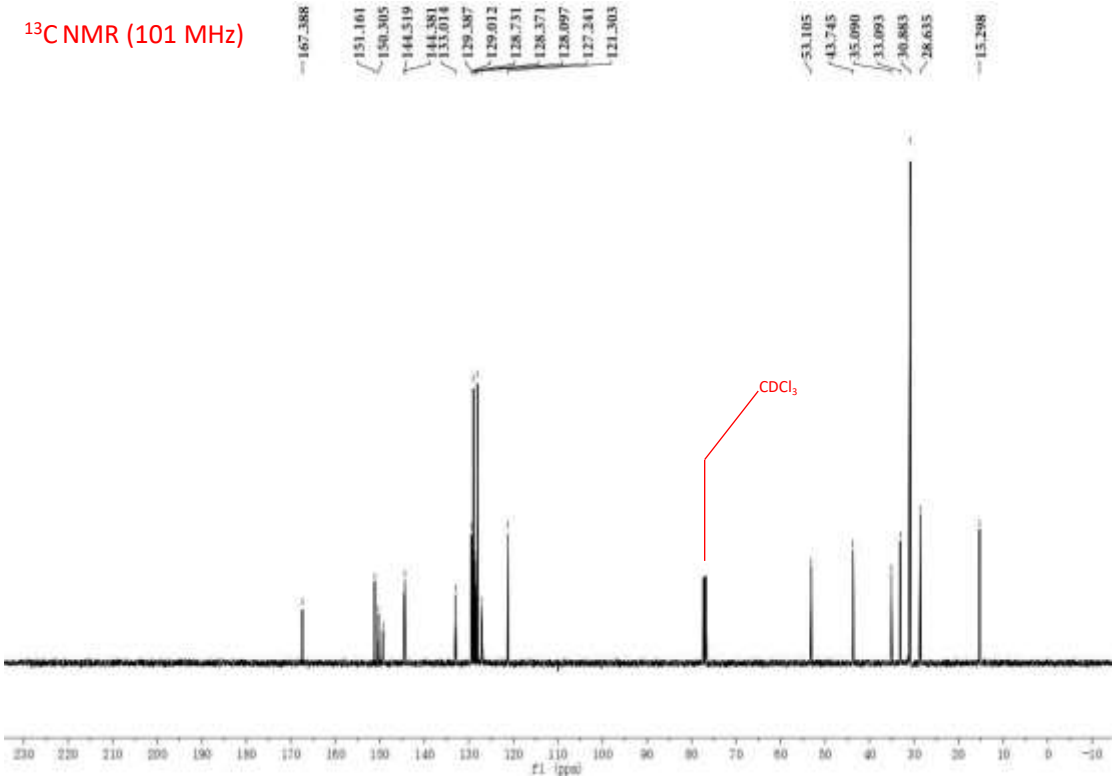


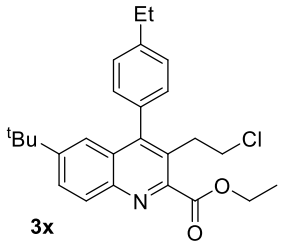


^{1}H NMR (400 MHz)



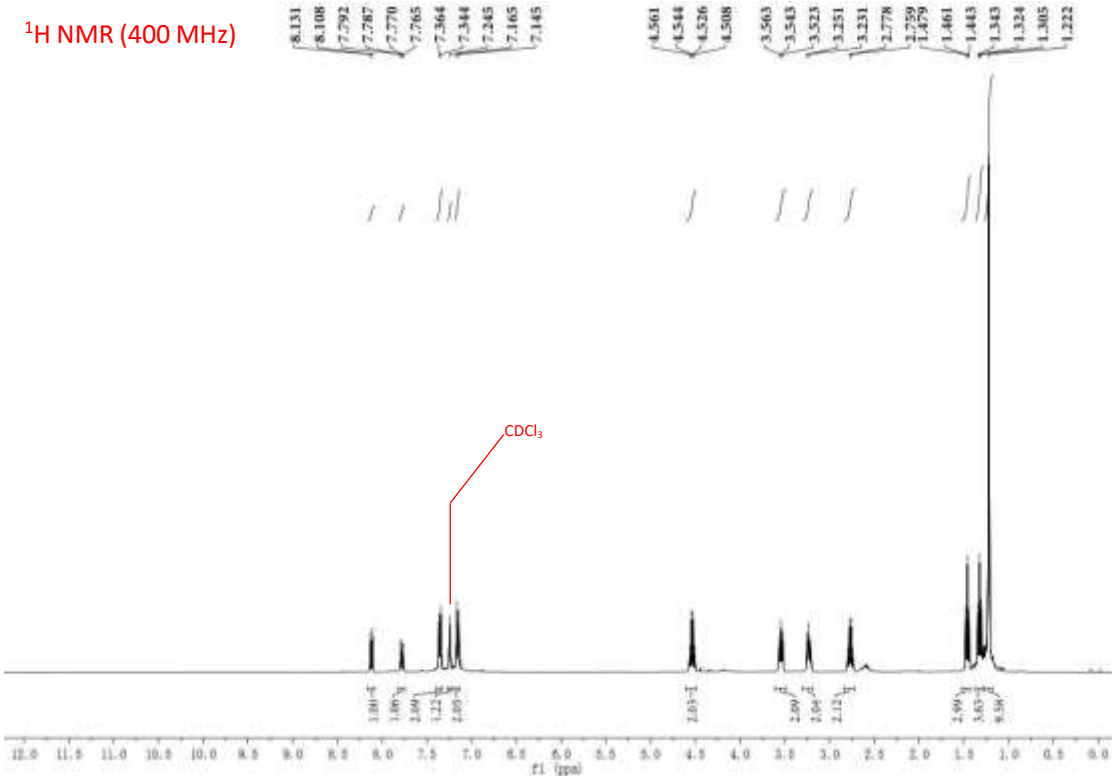
^{13}C NMR (101 MHz)



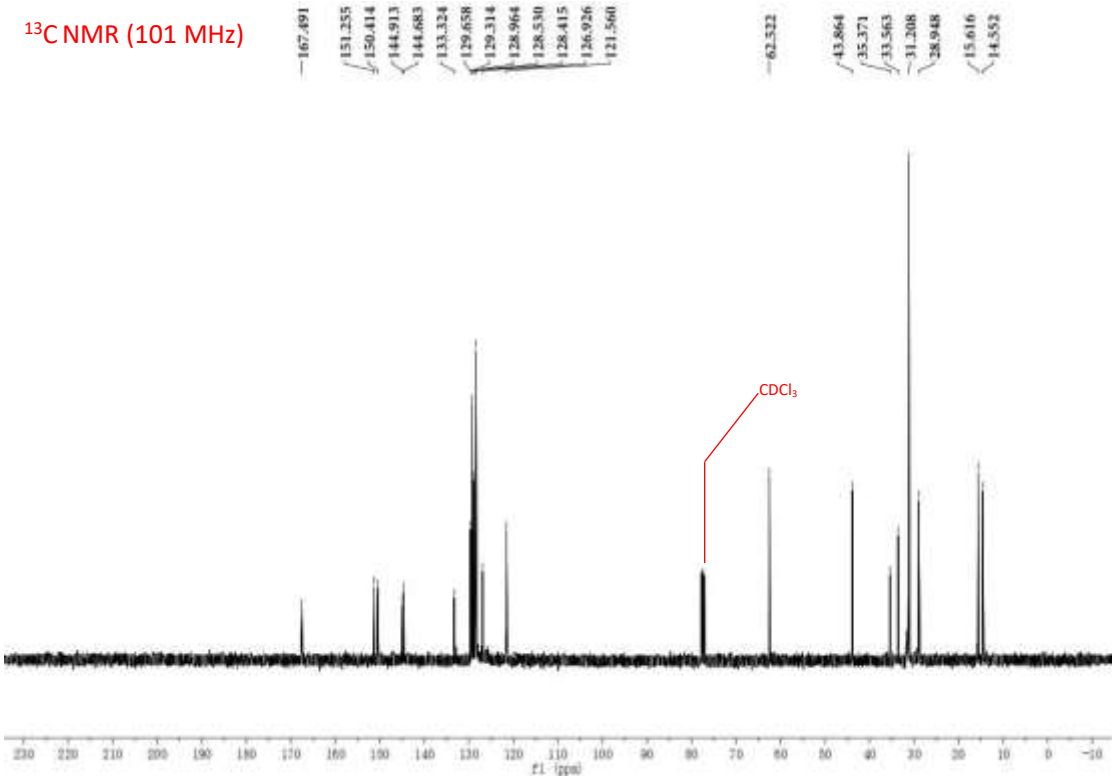


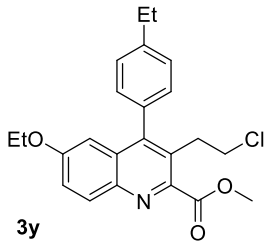
3x

^{1}H NMR (400 MHz)

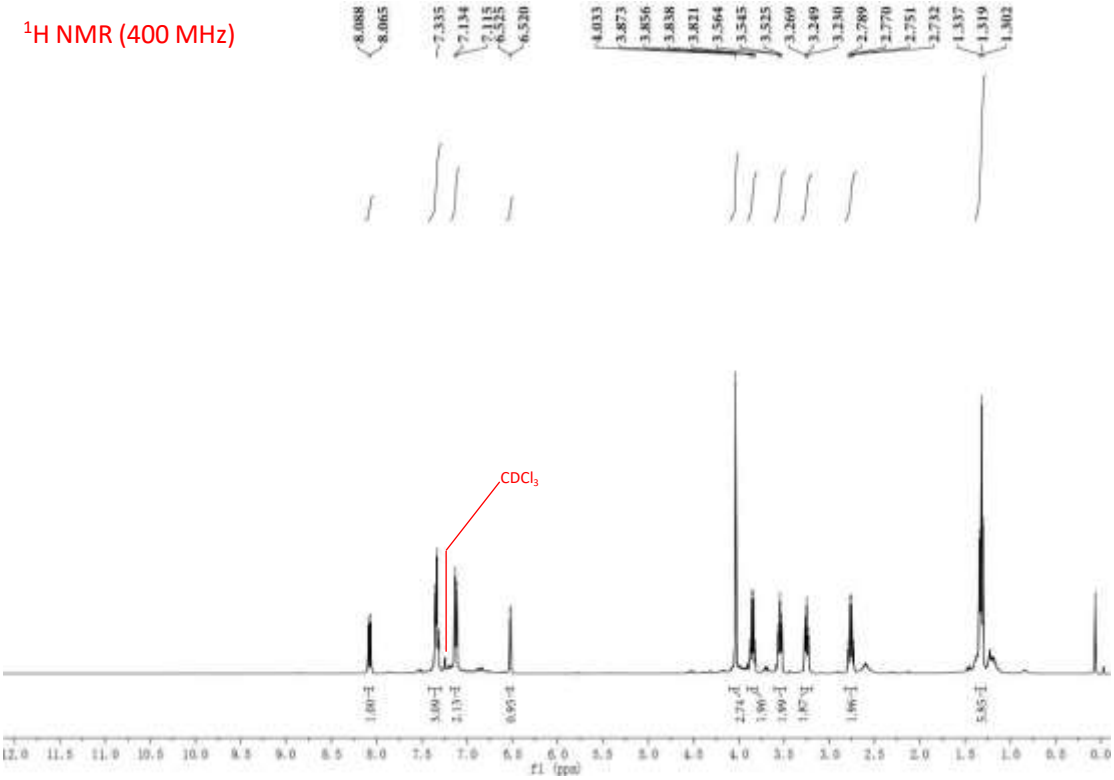


^{13}C NMR (101 MHz)

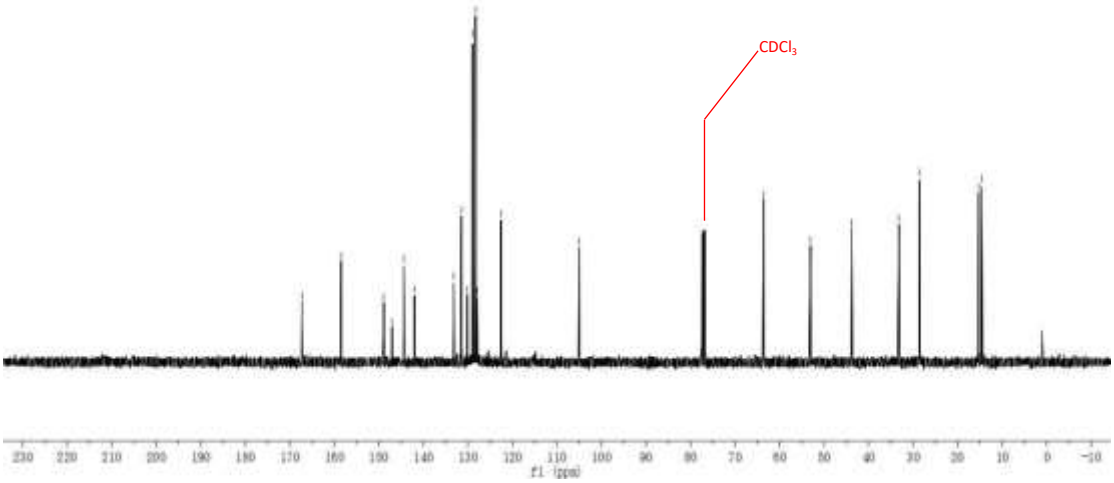


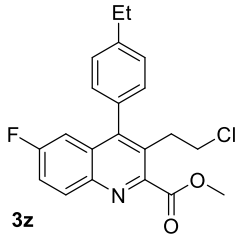


^{1}H NMR (400 MHz)

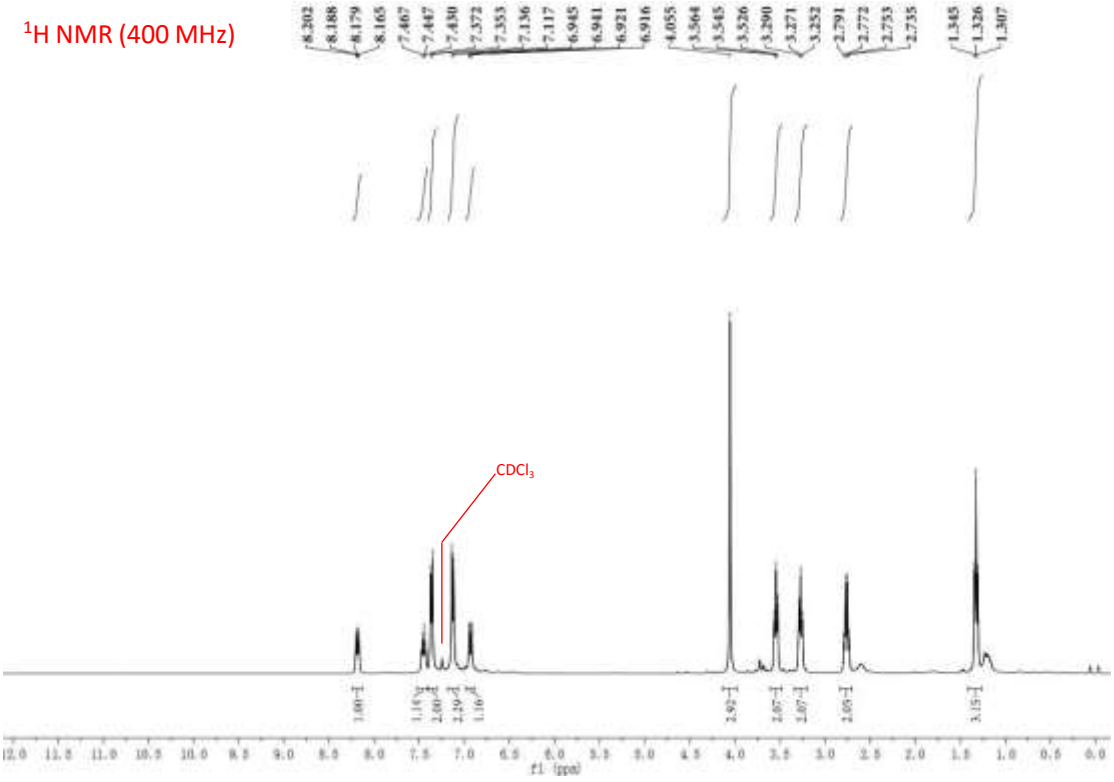


^{13}C NMR (101 MHz)

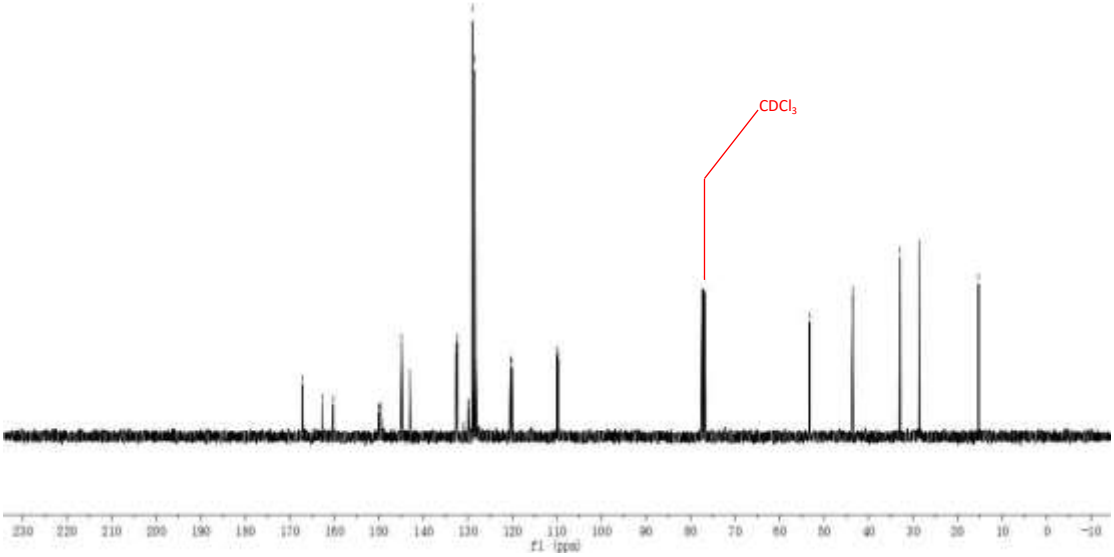


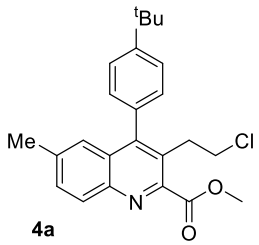


^{1}H NMR (400 MHz)

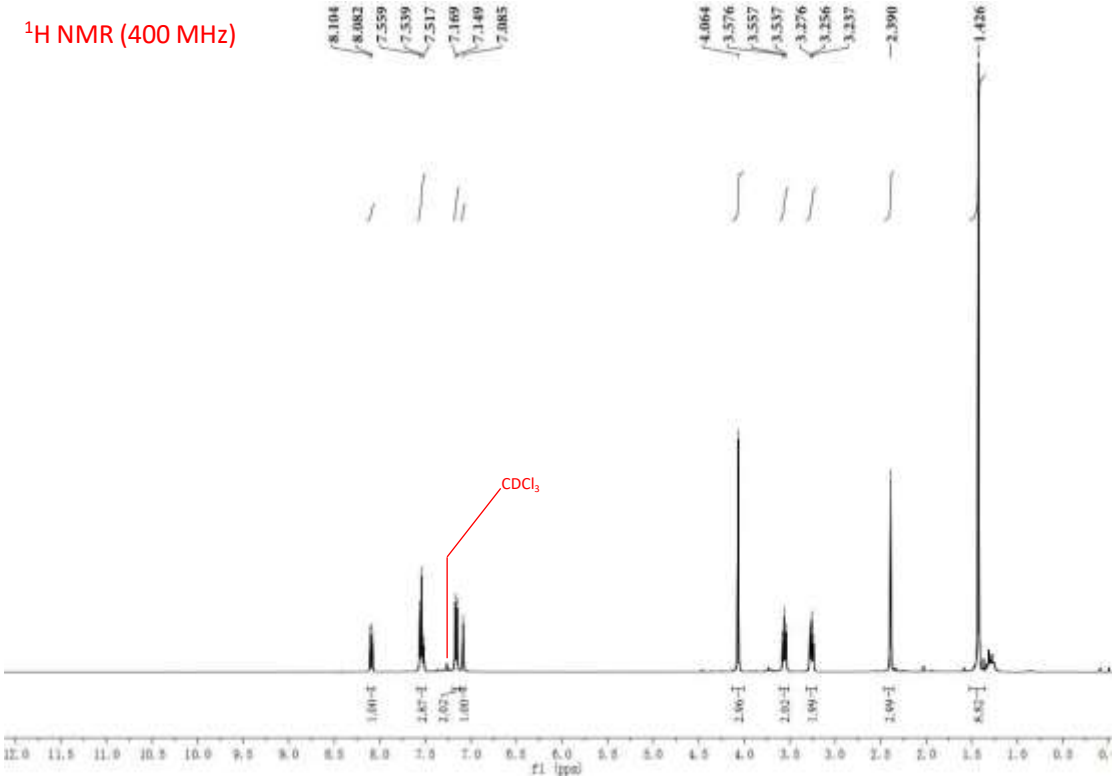


^{13}C NMR (101 MHz)

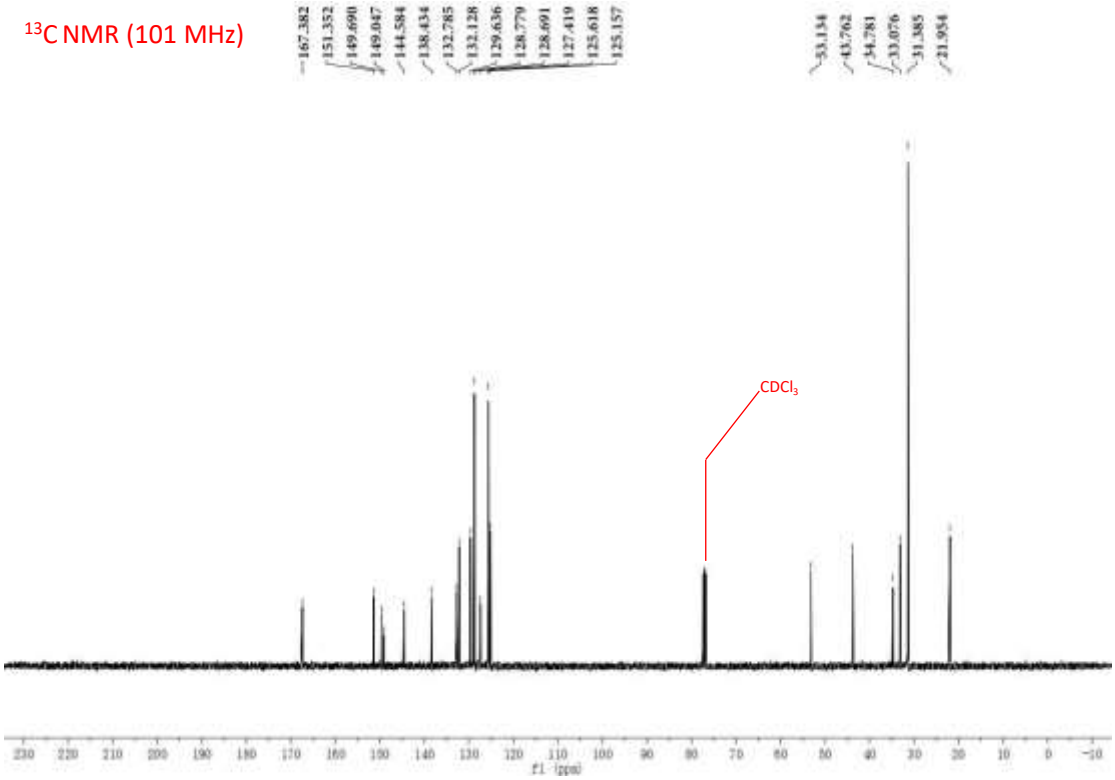


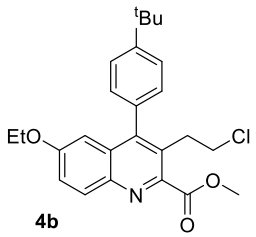


^{1}H NMR (400 MHz)

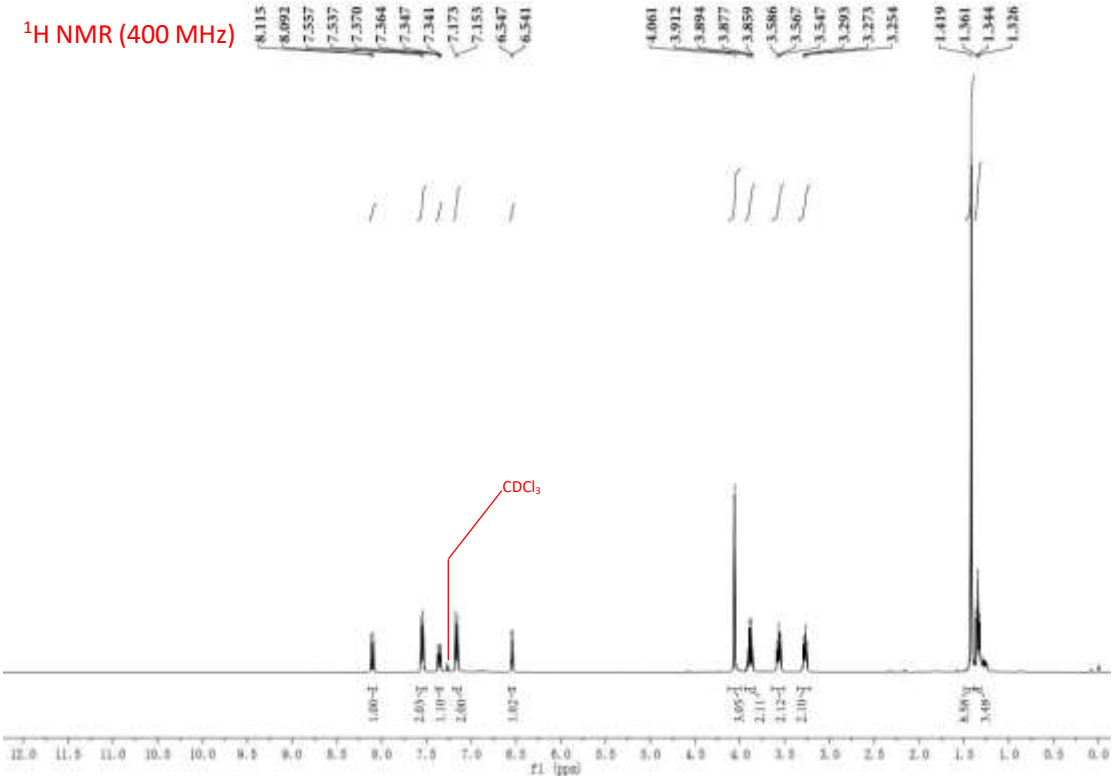


^{13}C NMR (101 MHz)

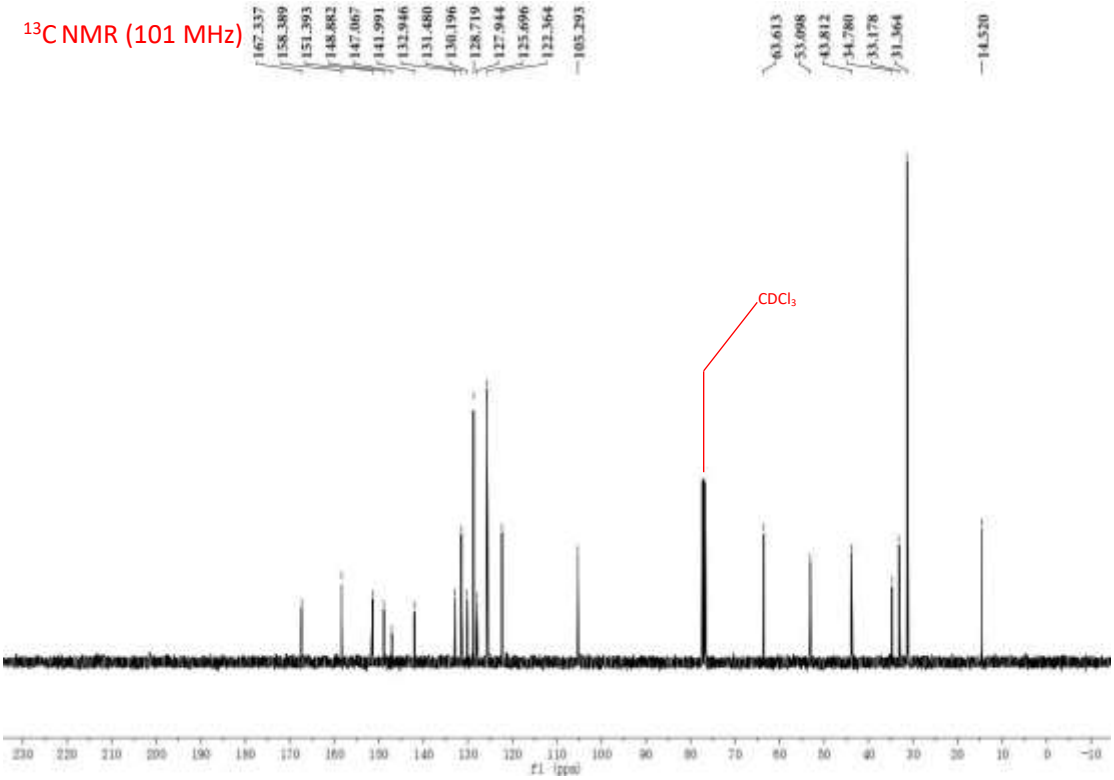


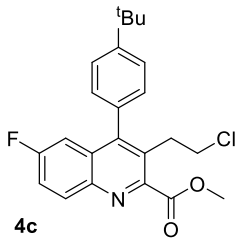


^{1}H NMR (400 MHz)



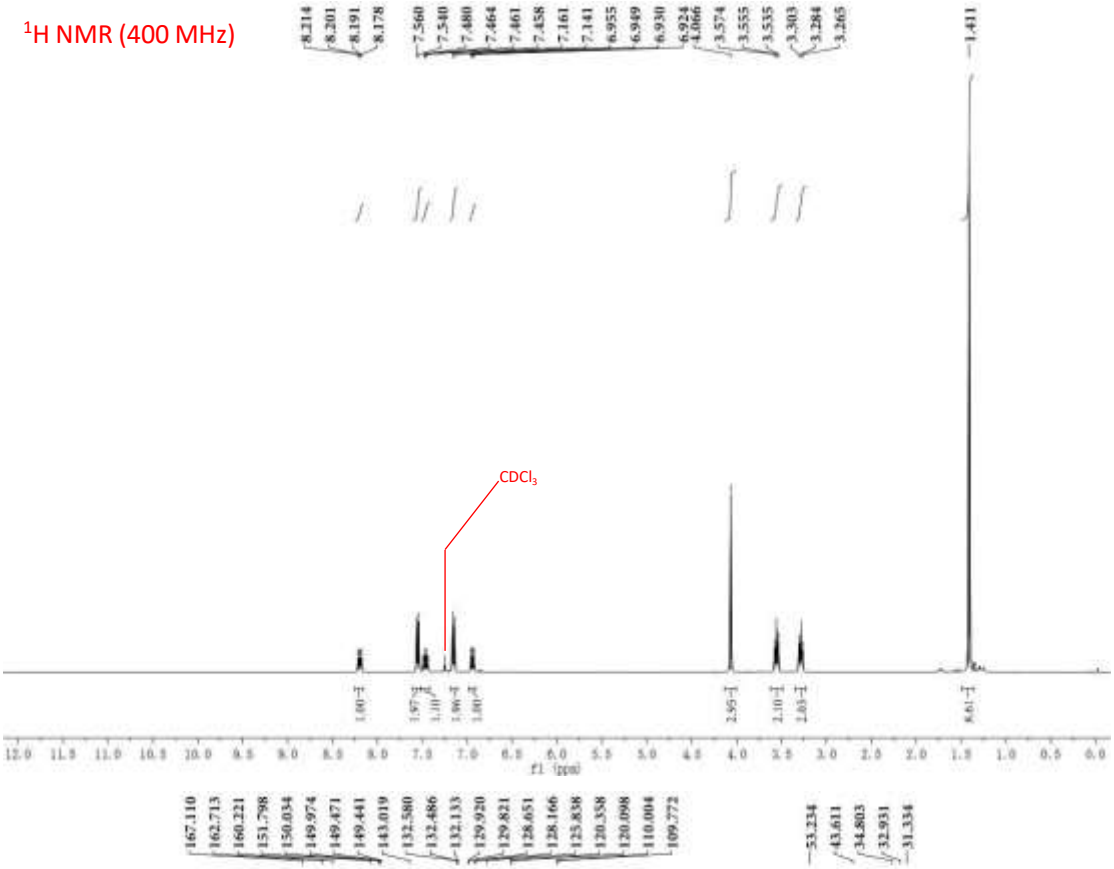
^{13}C NMR (101 MHz)



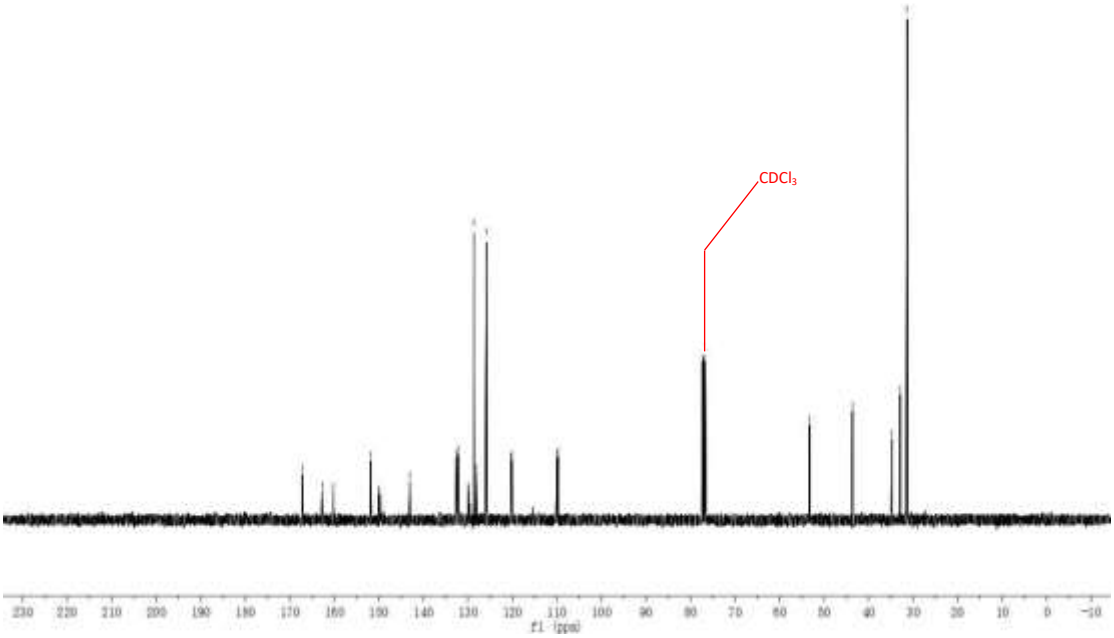


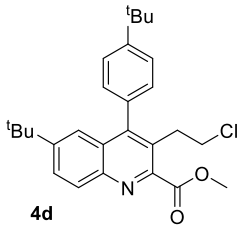
4c

^{1}H NMR (400 MHz)

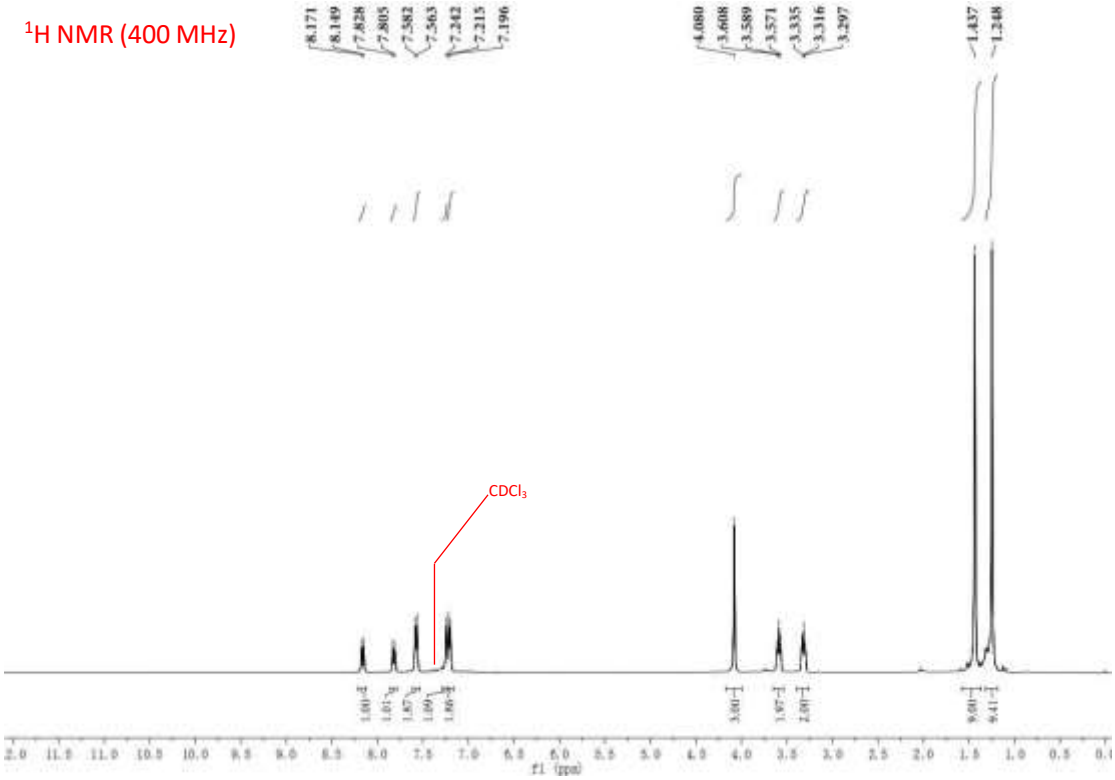


^{13}C NMR (101 MHz)

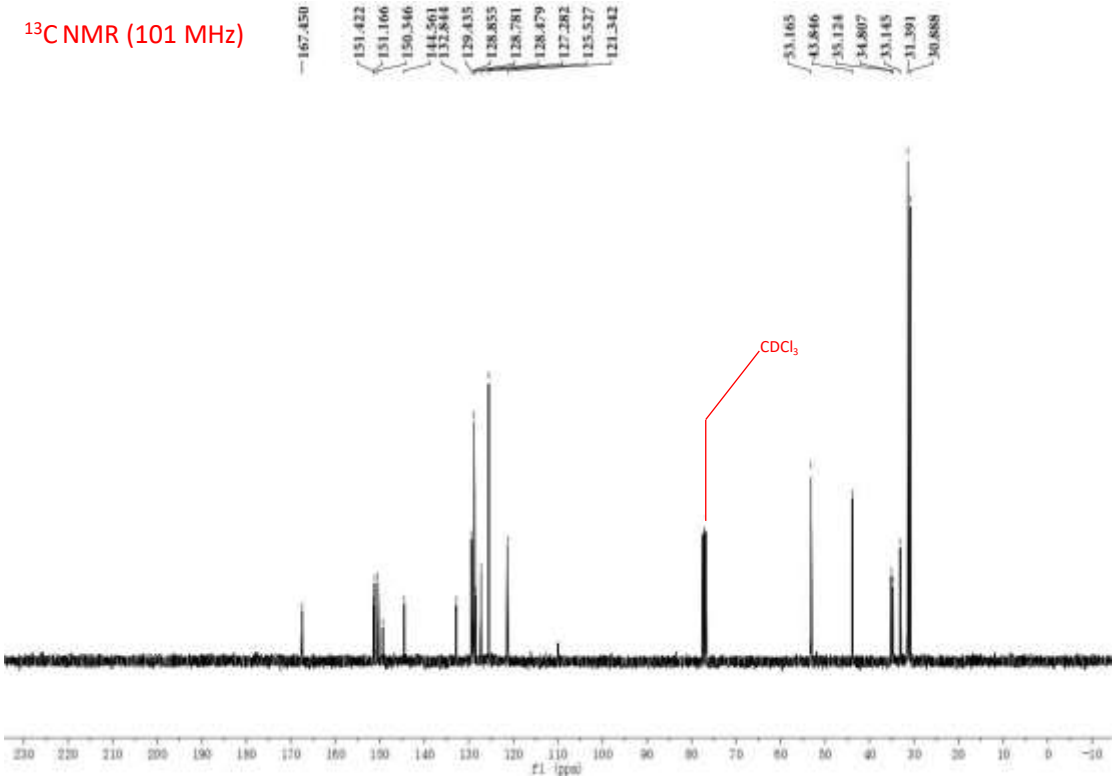


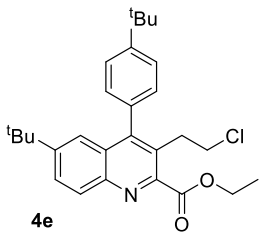


^{1}H NMR (400 MHz)

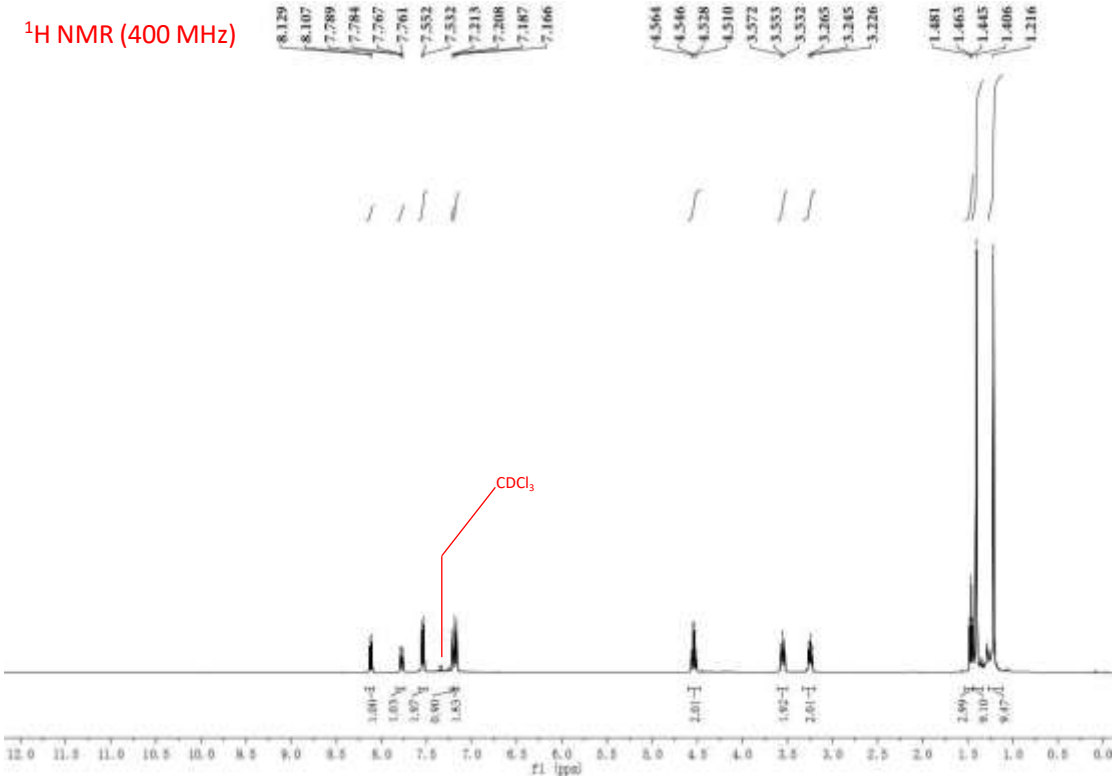


^{13}C NMR (101 MHz)

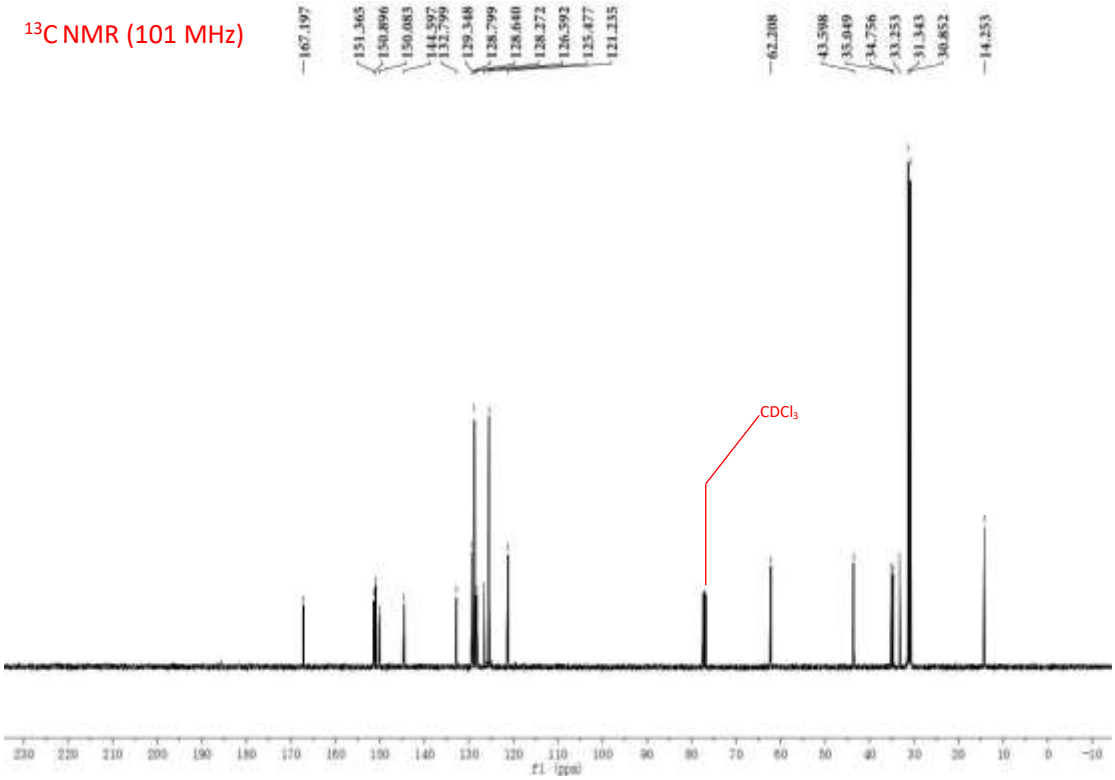


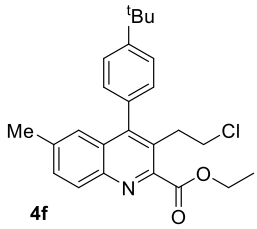


^{1}H NMR (400 MHz)



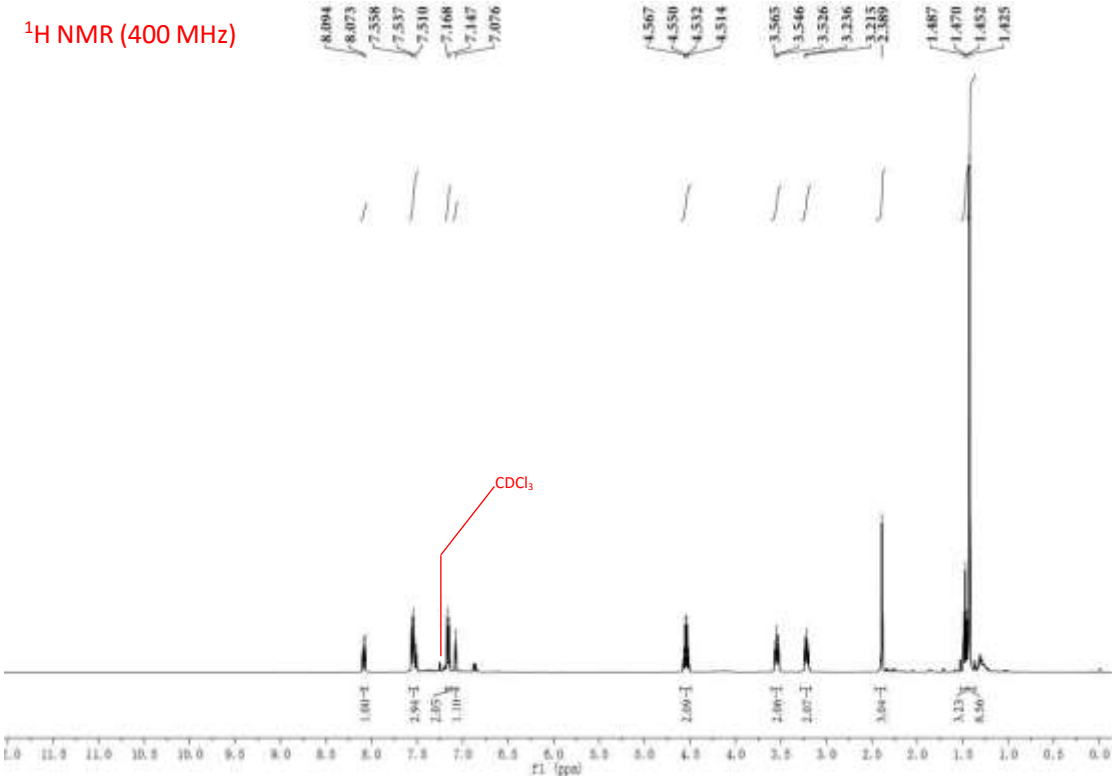
^{13}C NMR (101 MHz)



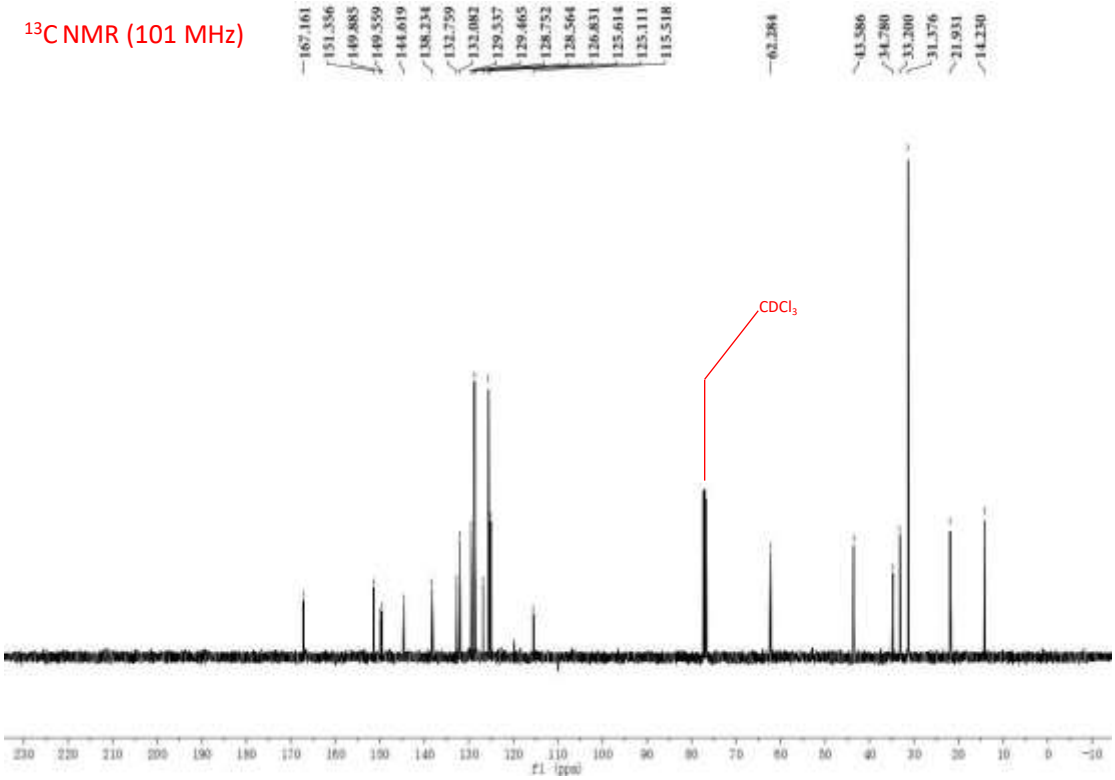


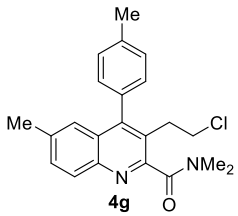
4f

^{1}H NMR (400 MHz)

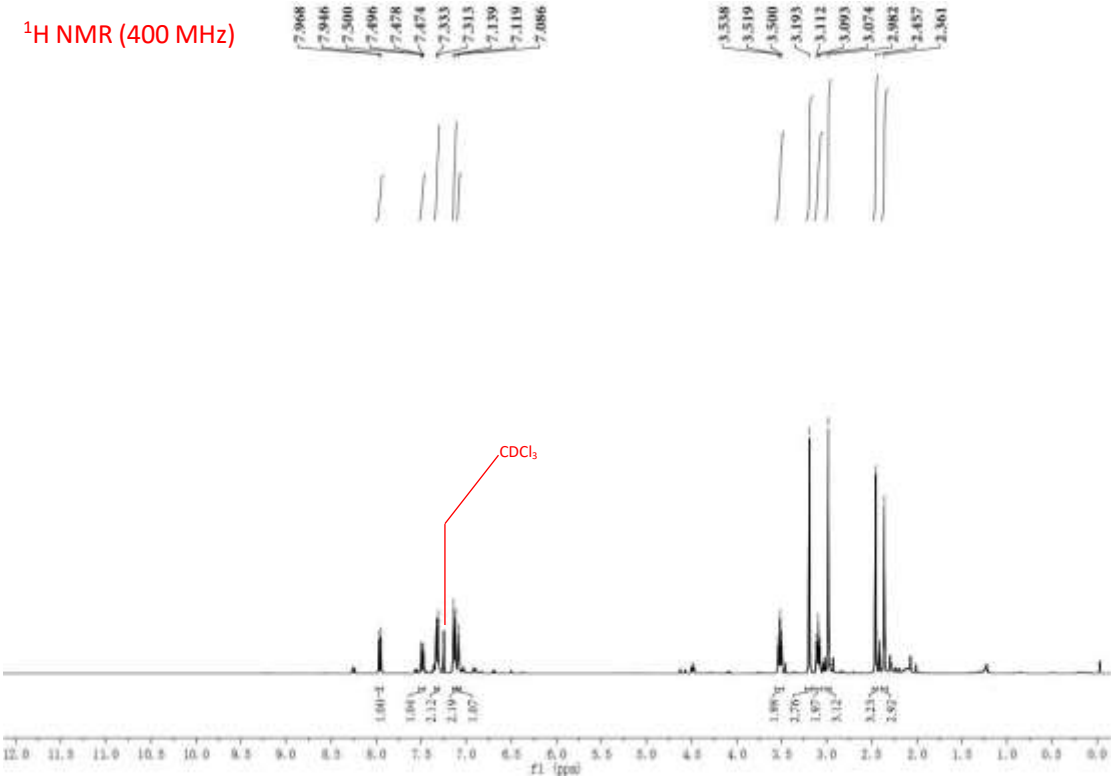


^{13}C NMR (101 MHz)

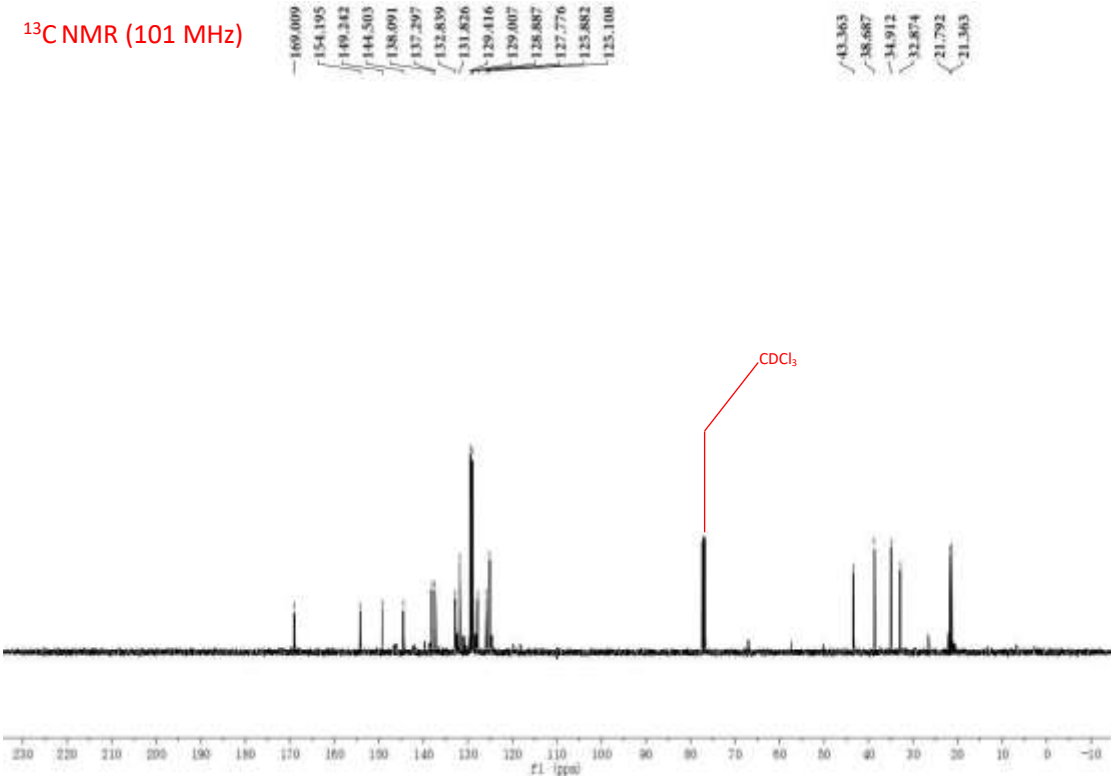


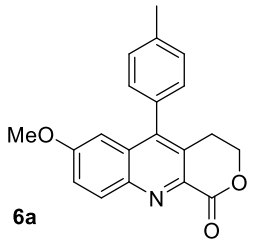


^{1}H NMR (400 MHz)



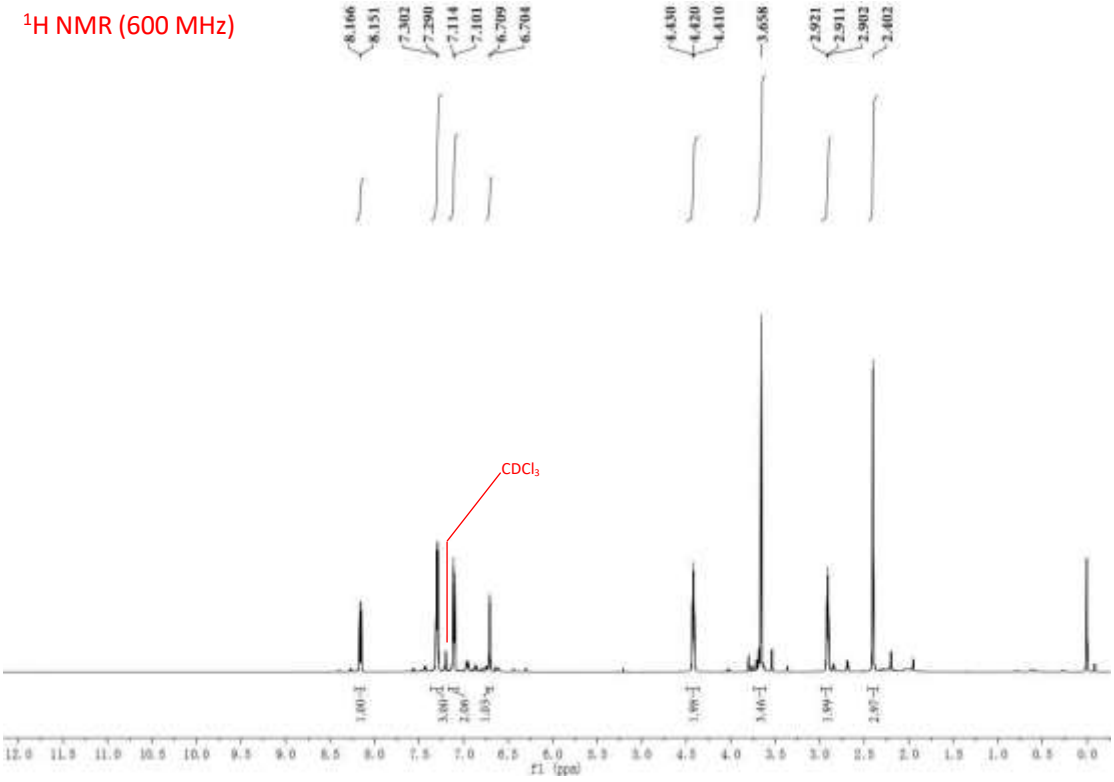
^{13}C NMR (101 MHz)



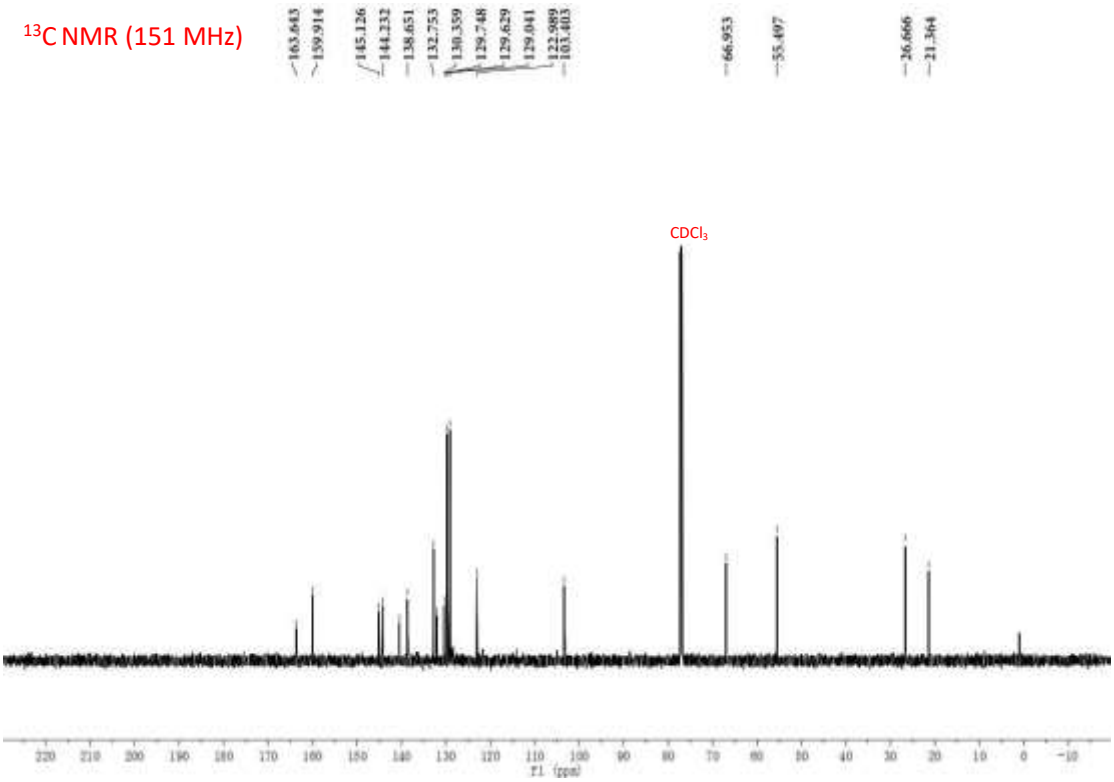


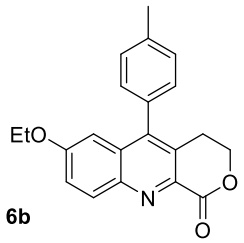
6a

^{1}H NMR (600 MHz)



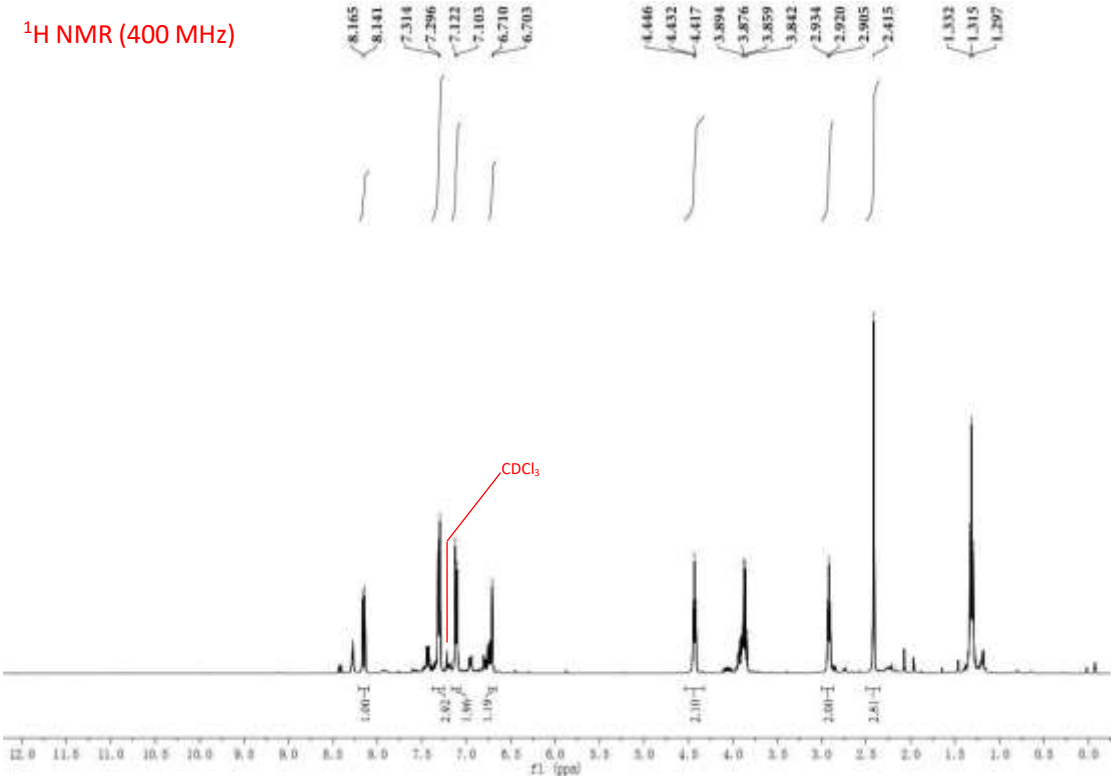
^{13}C NMR (151 MHz)



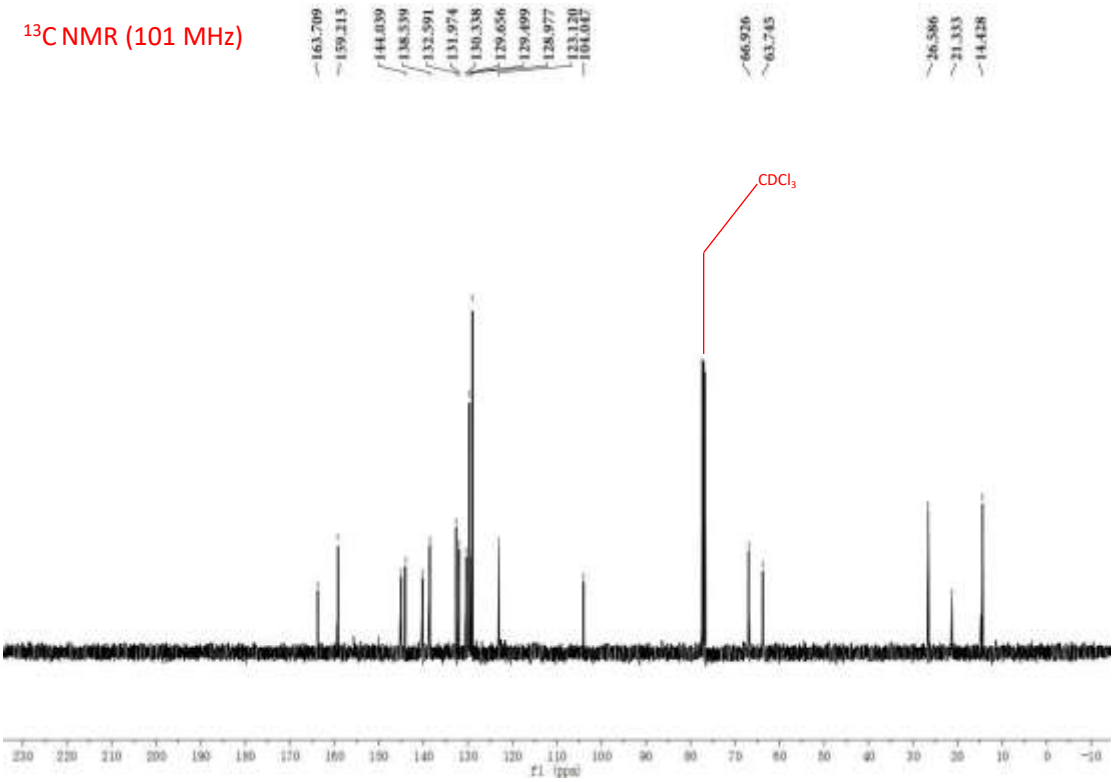


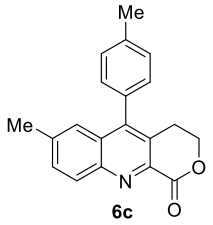
6b

^{1}H NMR (400 MHz)

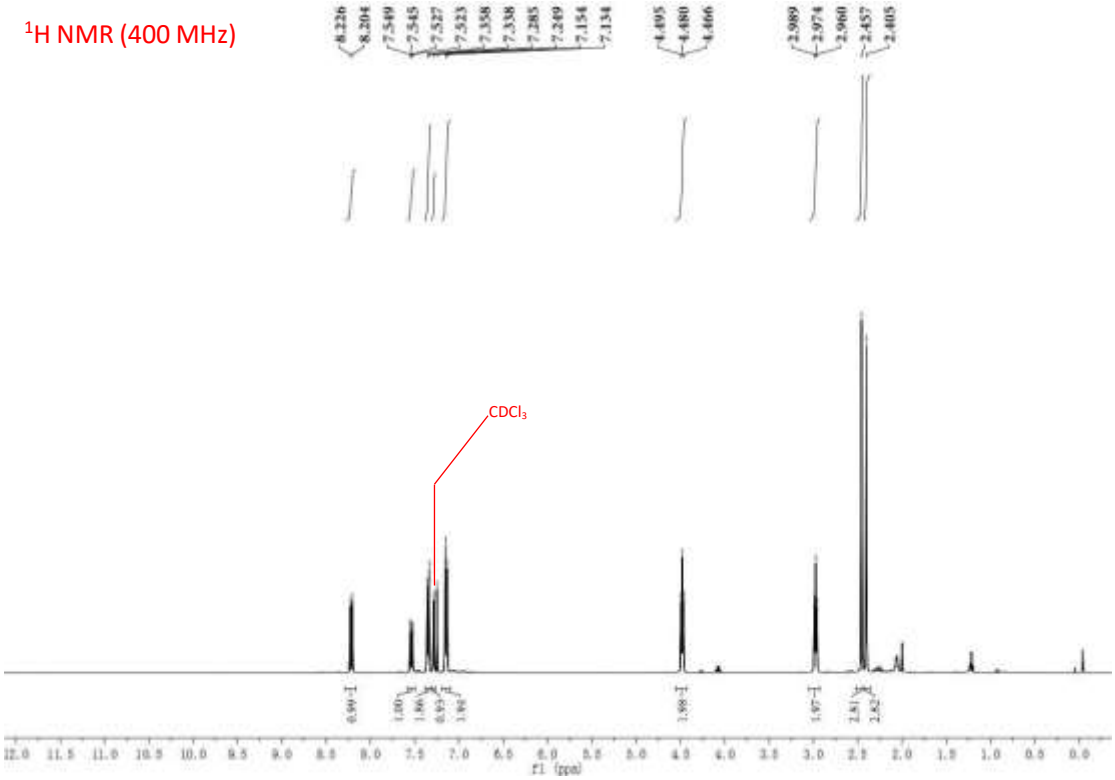


^{13}C NMR (101 MHz)

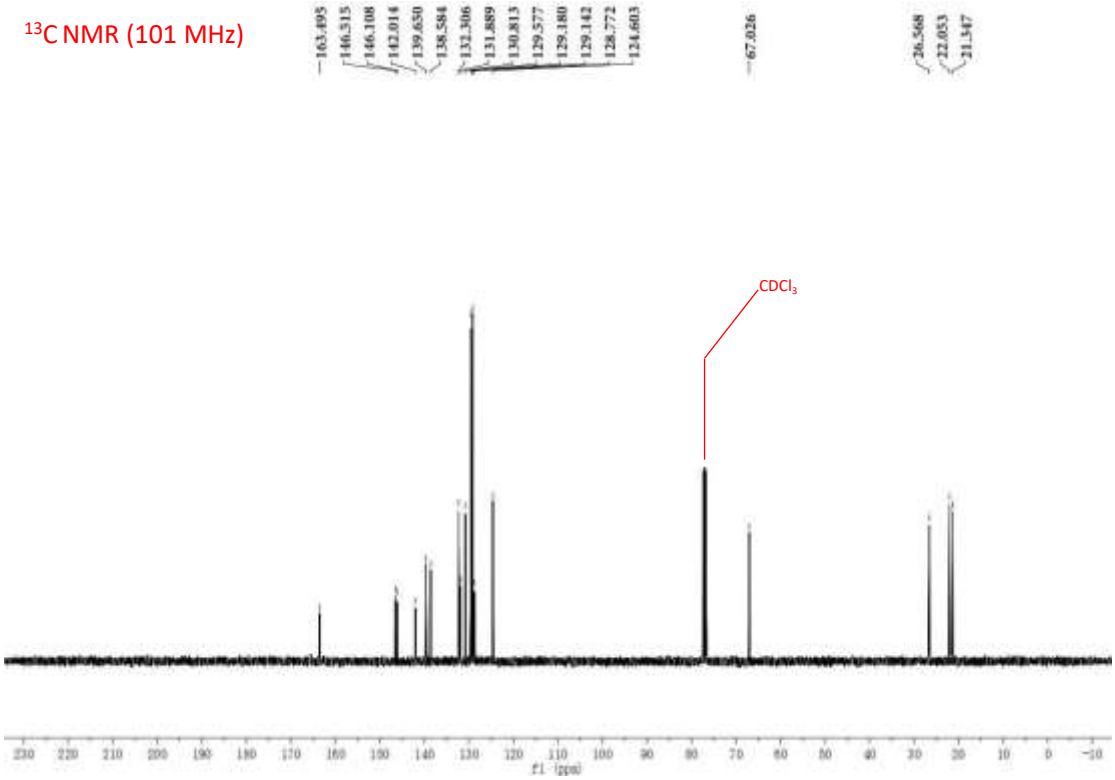


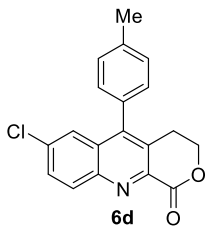


^{1}H NMR (400 MHz)



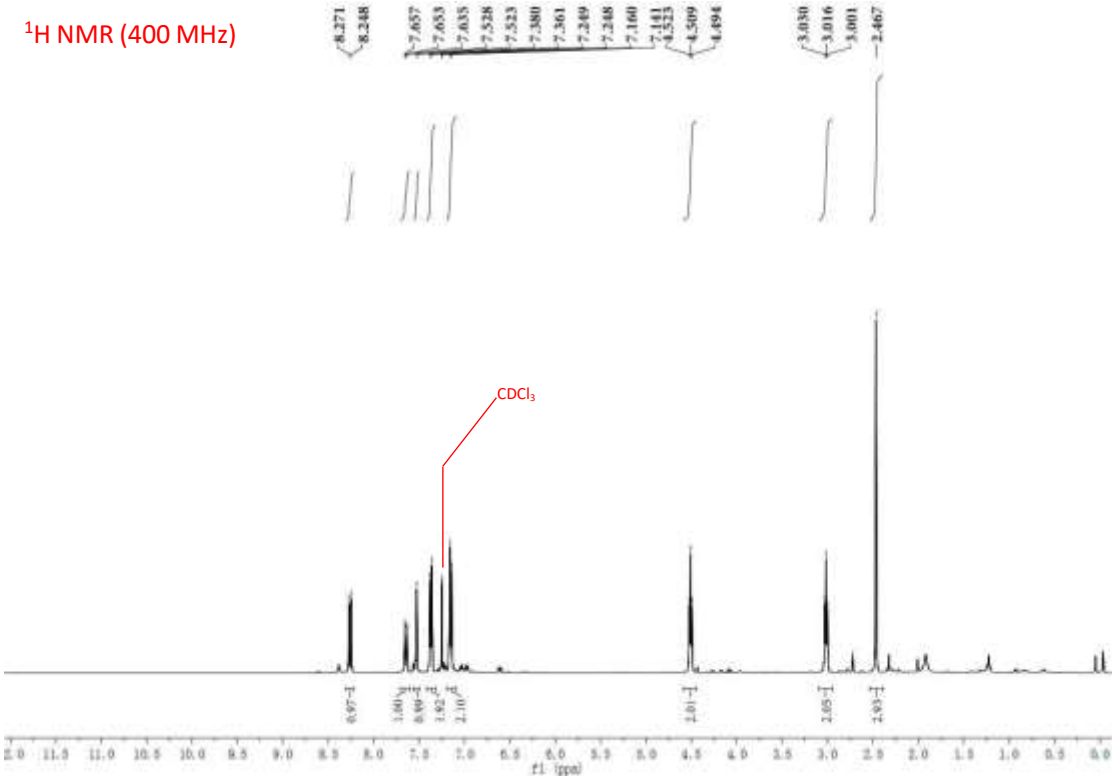
^{13}C NMR (101 MHz)



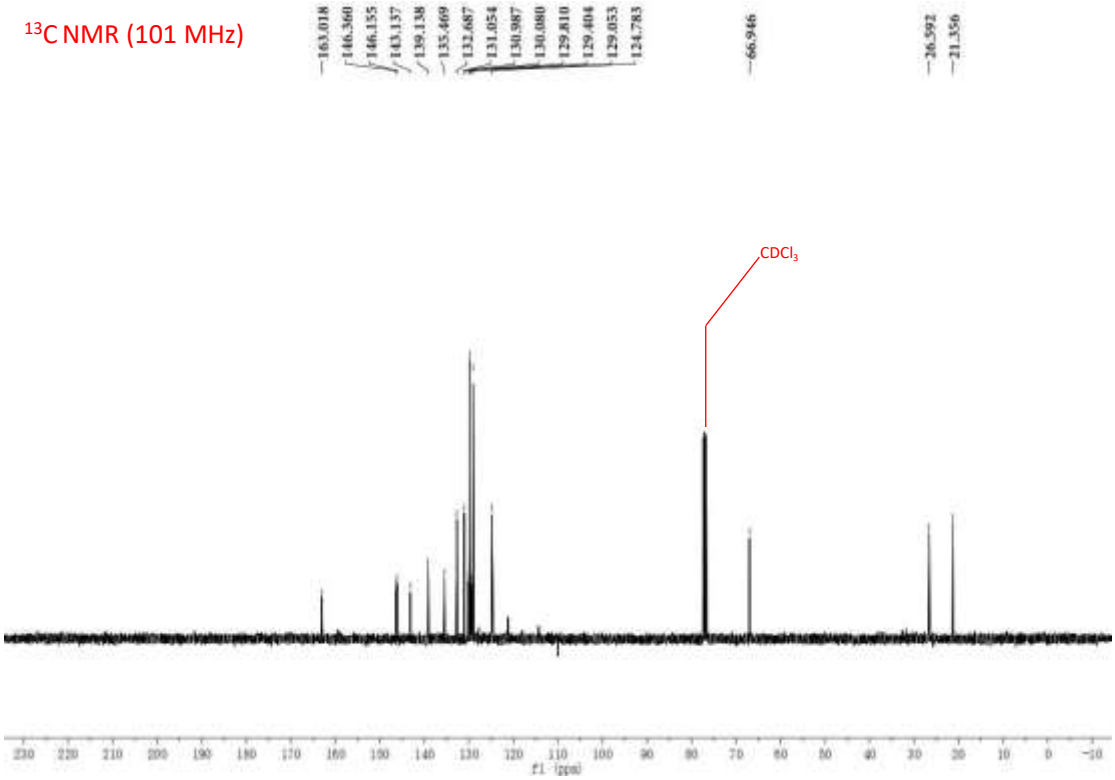


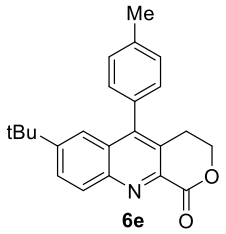
6d

^{1}H NMR (400 MHz)



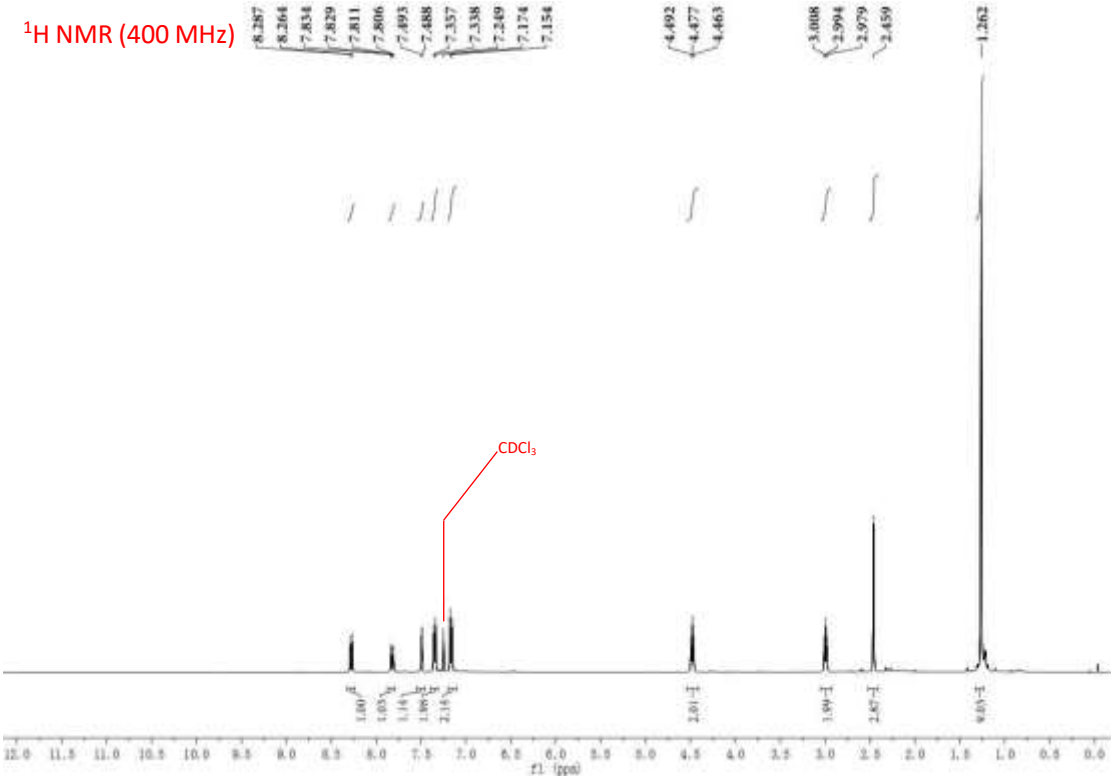
^{13}C NMR (101 MHz)



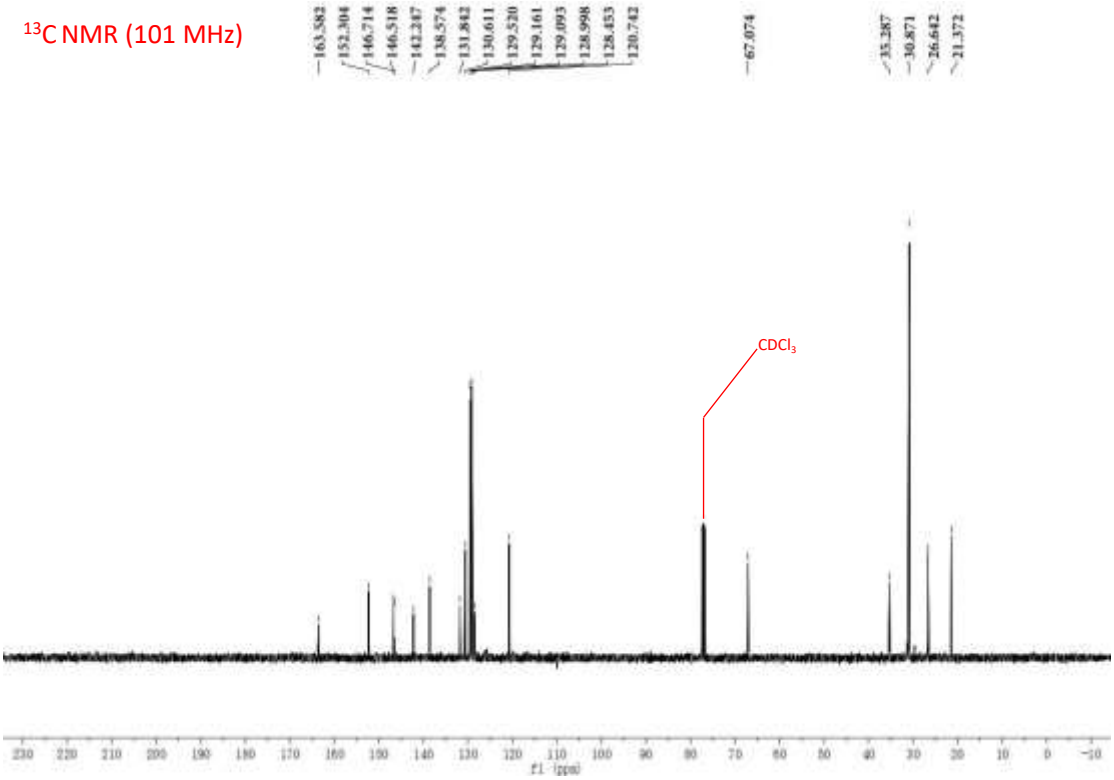


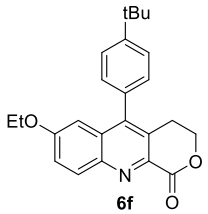
6e

^{1}H NMR (400 MHz)

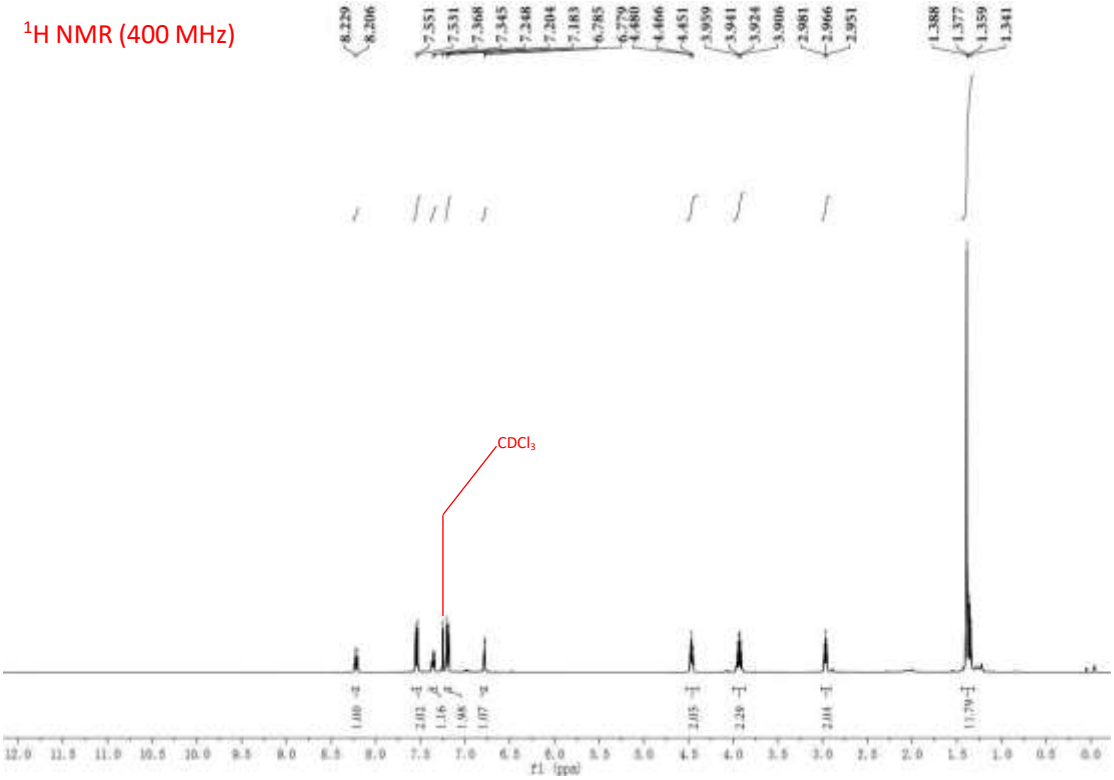


^{13}C NMR (101 MHz)

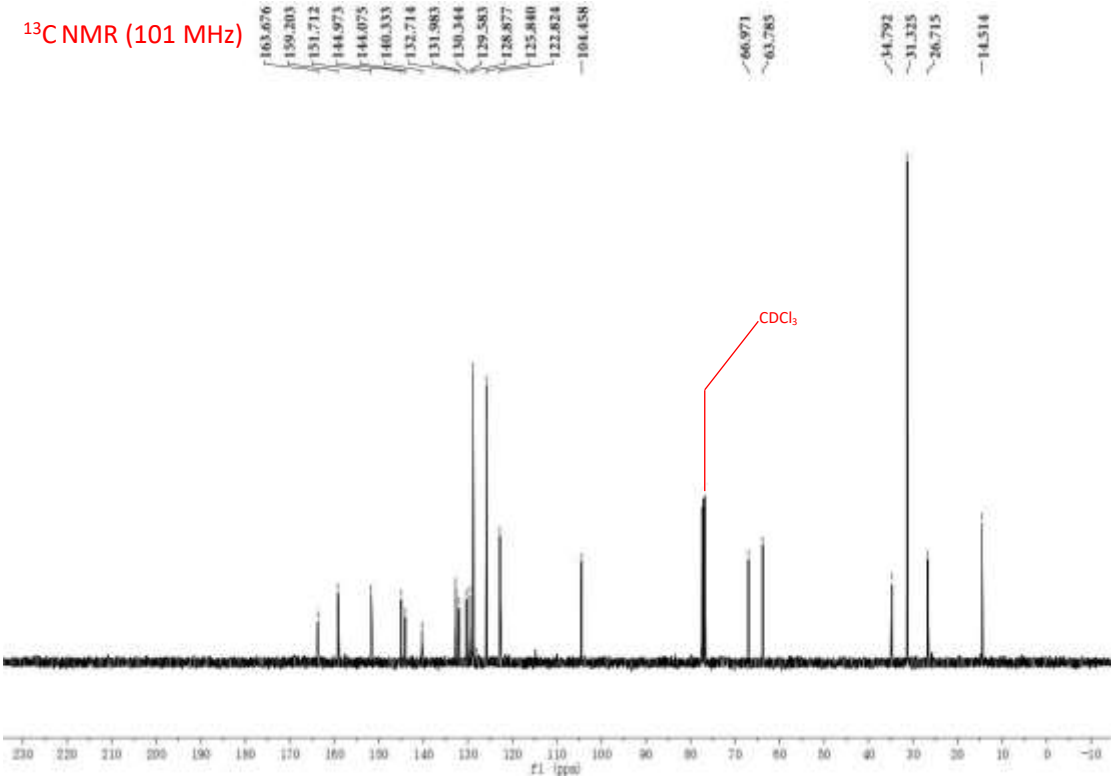


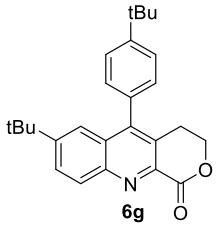


^{1}H NMR (400 MHz)



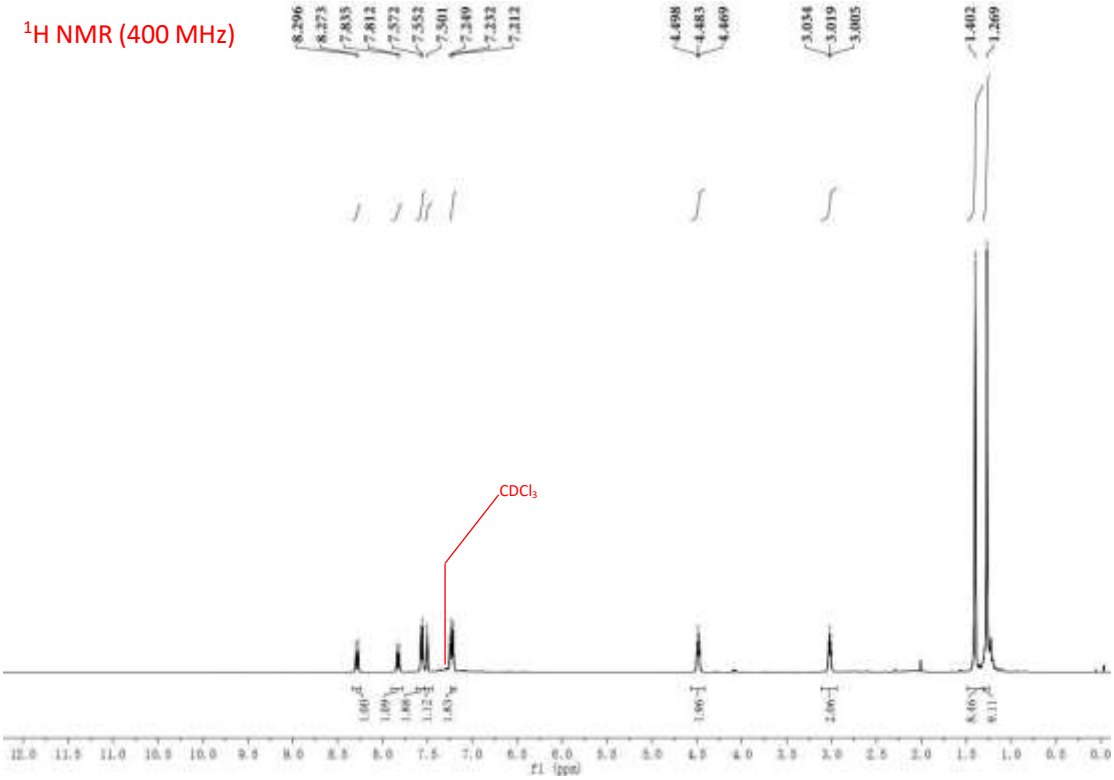
^{13}C NMR (101 MHz)



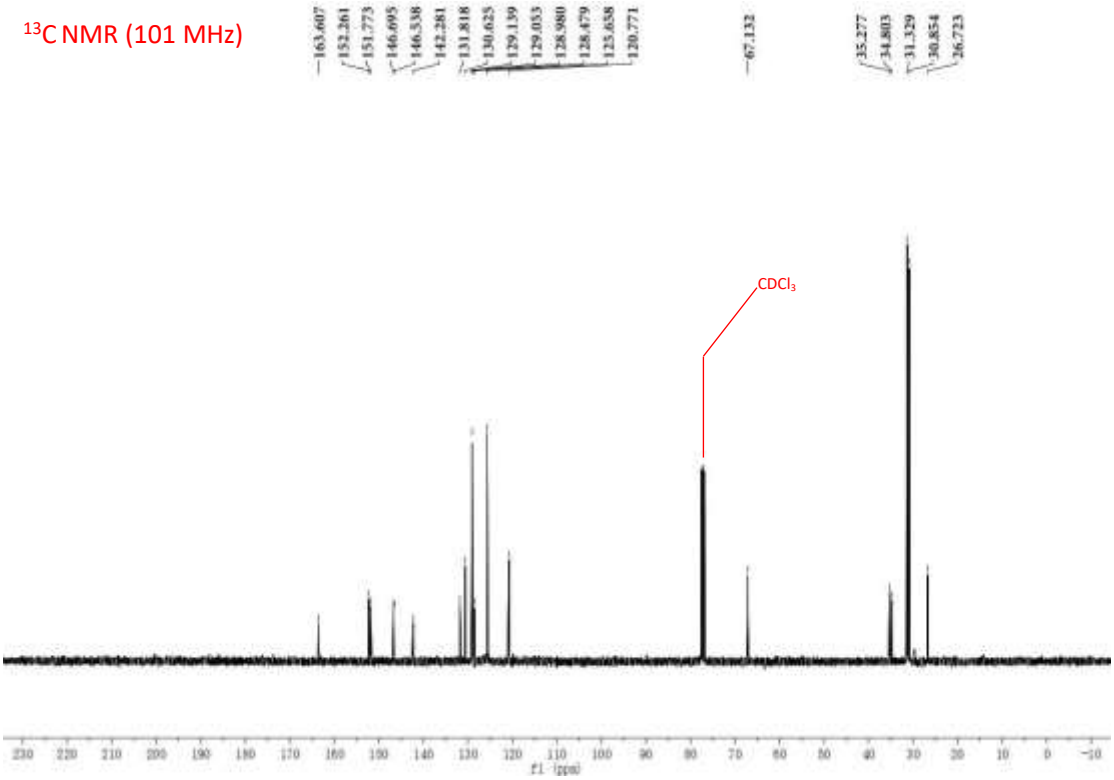


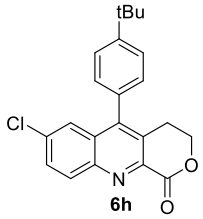
6g

^{1}H NMR (400 MHz)



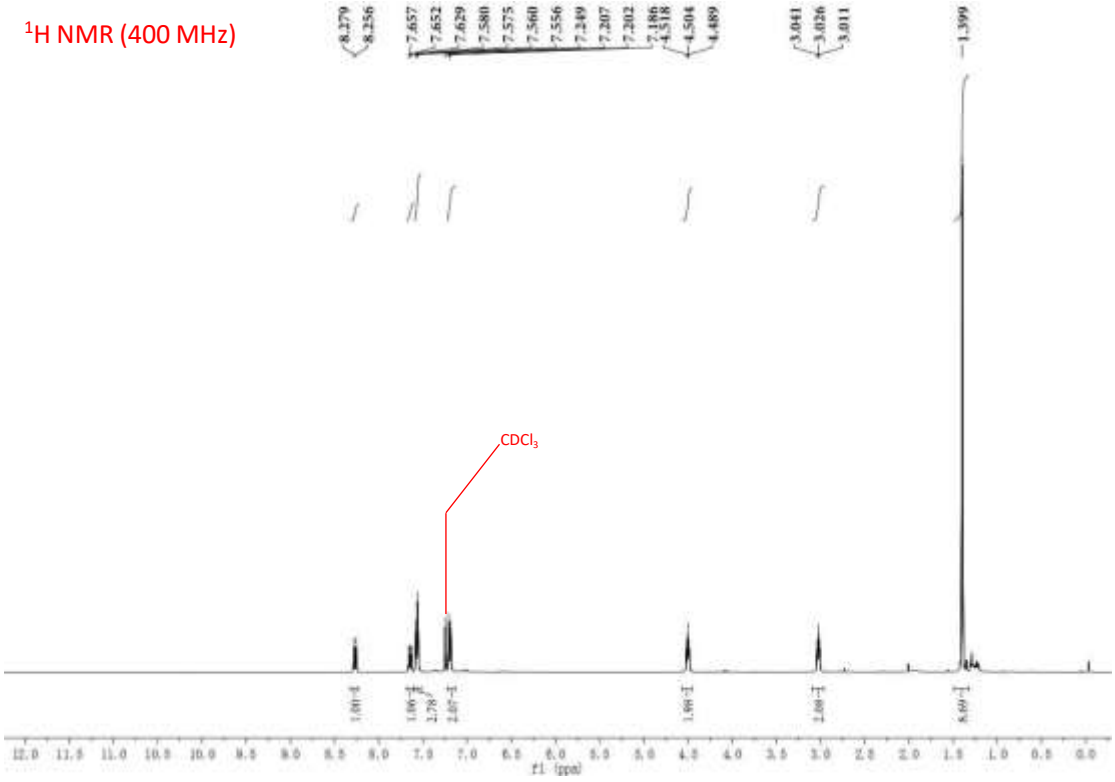
^{13}C NMR (101 MHz)



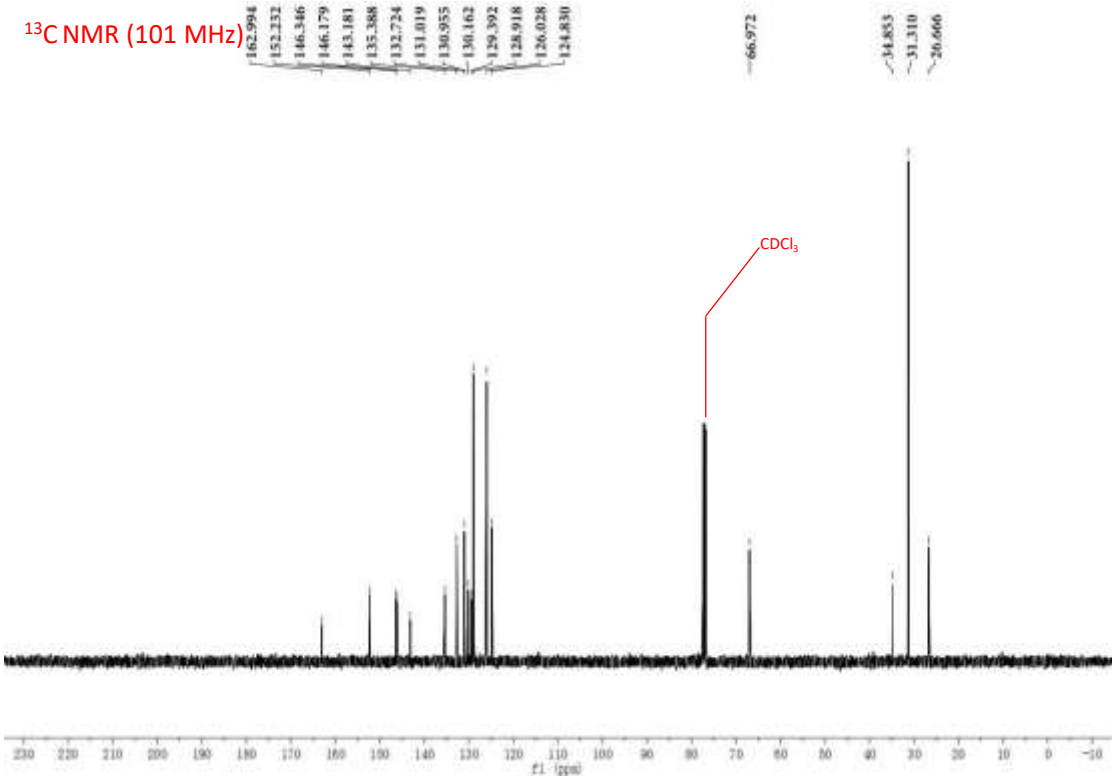


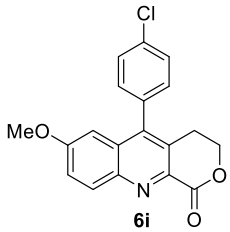
6h

^{1}H NMR (400 MHz)



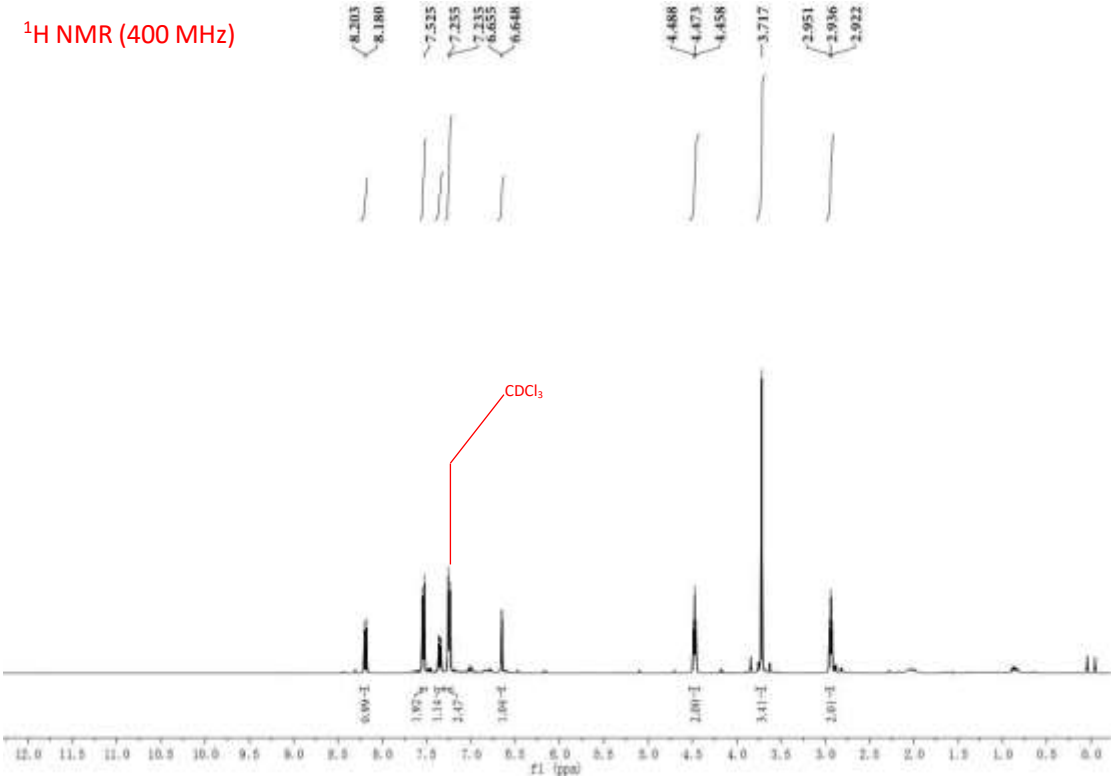
^{13}C NMR (101 MHz)



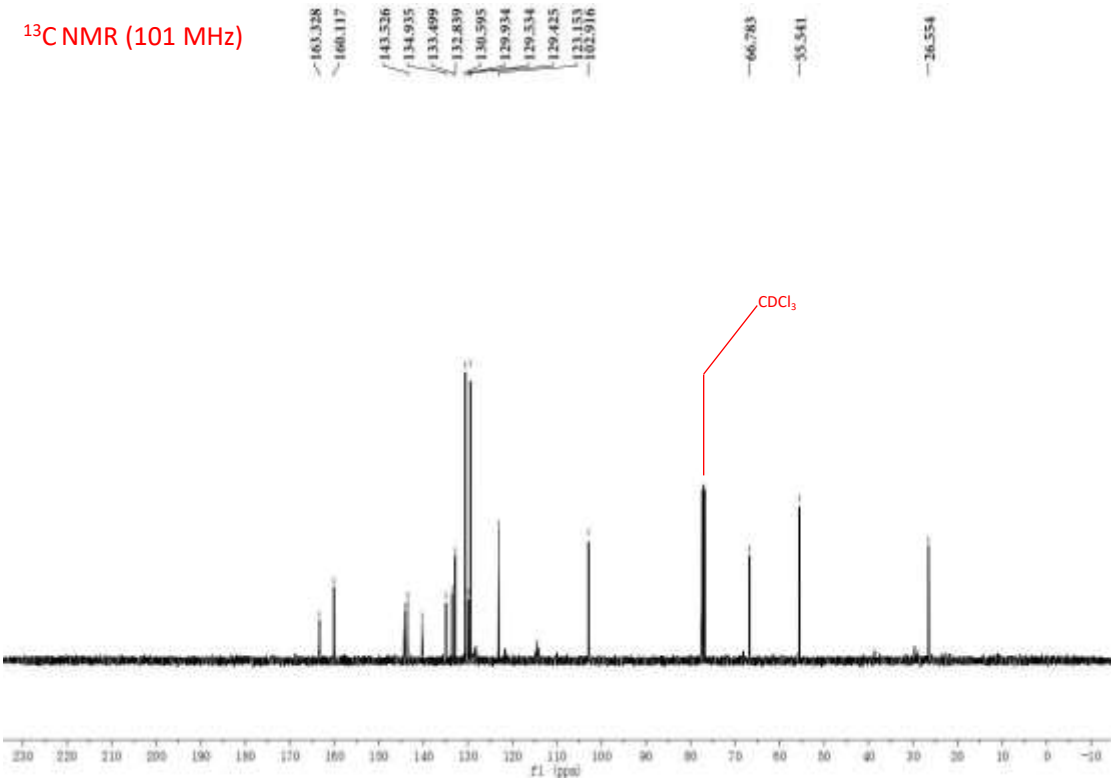


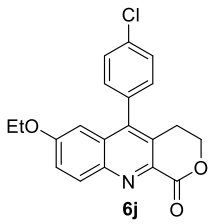
6i

^{1}H NMR (400 MHz)



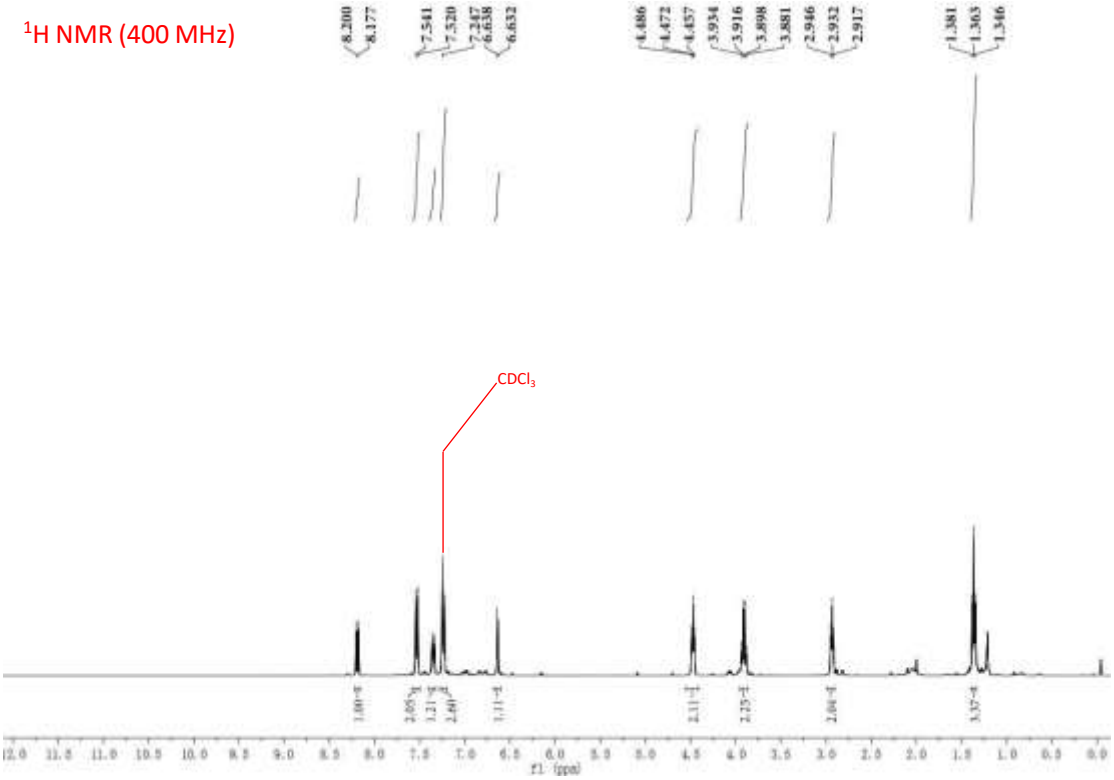
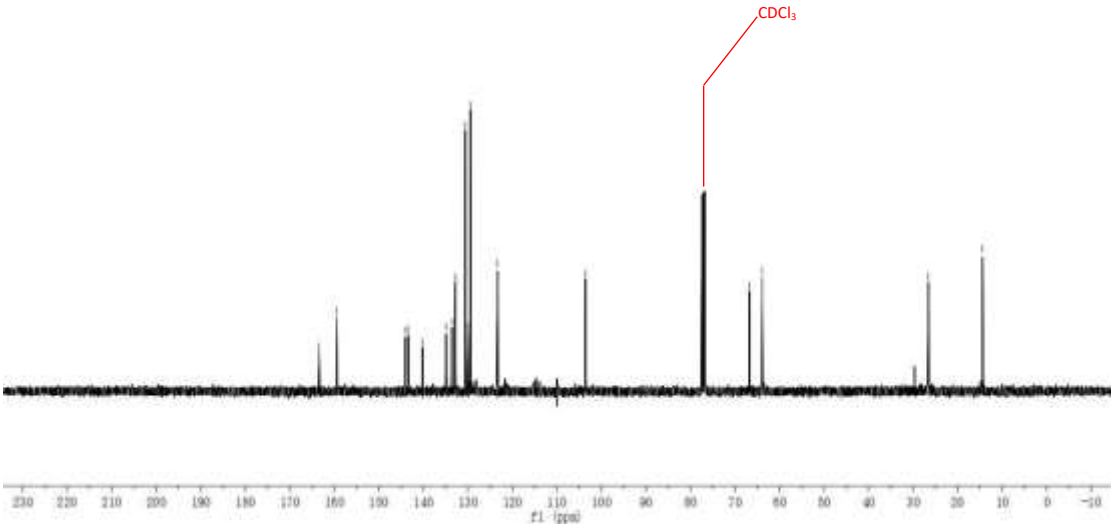
^{13}C NMR (101 MHz)





6j

^{1}H NMR (400 MHz)



^{13}C NMR (101 MHz)